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Sediment concentration and turbidity changes during culvert removals

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Abstract

The concentrations of sediment and turbidity in stream water were monitored during culvert removals to determine the short term effects of road obliteration. Sediment concentration was measured at 11 stream crossings among two locations in Idaho and one in Washington. Sediment concentration immediately below the culvert outlet exceeded levels above the culvert outlet by at least three orders of magnitude at all stream crossings. Sediment yields ranged from 170 to less than 1 kg in the 24-h period following culvert removal. Turbidity exceeded the regulatory limits during culvert removal at all locations monitored in this study and remained above the limits beyond the monitoring periods of 24 h at four of the locations. Sediment concentrations 100 m downstream of the culvert outlet were reduced by an order of magnitude, but did not change the turbidity values sufficiently to meet regulatory limits. Sediment concentrations an average of 810 m downstream of the culvert outlet were similar to sediment concentrations above the culvert for the entire excavation period and turbidity regulations were met. Mitigation consisting of two straw bales placed in the stream caused a significant reduction in sediment yield from an average of 67 kg to an average of 1.6 kg.

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1. Introduction

Between 1950 and 1990, the number of unpaved forest roads constructed each year on national forest lands for timber harvesting, mining and forest management activities increased. In 2005, the forest road inventory indicated 609 300 km of roads on forest lands managed by the United States Forest Service (USFS). Most unpaved USFS roads created for past forest operations are no longer used for their original purposes and less than 20% are maintained according to originally specified safety and environmental standards (USDA Forest Service, 2002). Unmaintained forest roads can become unstable, present safety hazards, and increase surface

erosion and sediment loss from landslides during large storms.

Removing roads from service, or decommissioning roads, is an increasingly common management alternative applied on roads with low resource management priority, high risk of failure, or in environmentally sensitive areas. Methods of road decommissioning range from simply blocking the road entrance to completely removing and recontouring the former road surface. Road obliteration is the most comprehensive degree of decommissioning and involves decompacting the road surface (road ripping), removing culverts, re-establishing stream channels, and reshaping the roadbed to match the hillside contour.

The first extensive road obliteration operations took place in Redwood National Park where chronic landslides in the Redwood Creek watershed prompted intense mitigation of old, unstable logging roads. Between the years of 1978 and 1992, over 300 km of roads were obliterated to reduce sediment delivery to downstream salmon habitat. When over 200 obliterated stream crossings were examined, following a 12-year storm event in

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1997 in the Redwood National Park. Madej (2001) determined that road obliteration greatly reduced long-term sediment yields compared to untreated roads. This study prompted many forest managers to apply road obliteration techniques on national forests. Since 1991, over 50 000 km of forest roads have been decommissioned on national forest lands (USDA Forest Service, unpublished data).

In addition to removing unstable fills, road obliteration increases infiltration, which helps reestablish vegetation and restore hillslope hydrology. Luce (1997) measured infiltration rates of 0–12 mm/h on road surfaces prior to ripping and infiltration rates of 14–31 mm/h following ripping. Foltz and Maillard (2003) measured an increase in infiltration from 2 to 10 mm/h in the 2–3 year period following road obliteration. While still far below infiltration rates of undisturbed forest floors, which range from 36 to 80 mm/h (Robichaud, 2000), increases in infiltration capacity following road ripping can decrease runoff events. Foltz and Maillard (2003) used computer modeling to demonstrate that the increased infiltration capacity from road obliteration in central Idaho could reduce the number of runoff events from three per year to one event every other year.

The studies by Madej, Luce, and Foltz and Maillard indicate potential long-term benefits resulting from road obliteration with decreased occurrence of road related landslides and increased infiltration capacity of road surfaces. However, short-term effects of road obliteration have not been quantified. As with any excavation activity, there is risk of erosion during and immediately after road obliteration before exposed soil is stabilized by revegetation. Road obliteration, particularly culvert removal, has the potential to degrade water quality substantially during excavation.

Culvert replacement has been studied more than the removal of culverts during road obliteration (Faurot, 2005; Jakober, 2002). The two are similar in that both involve potential diversion of the stream, removal of the fill, and removal of the existing culvert. In road obliteration, the streambed is prepared to receive the stream flow while in culvert replacement, a new culvert is placed in the streambed.

Faurot (2005) reported that 90% of the increased turbidity due to culvert replacement was believed to occur during the reintroduction of stream flow into the channel and that rain events during and after construction might mobilize some sediment into the stream. Each of these observations was based on opinions by experienced field personnel rather than measurements. Jakober (2002) studied a culvert replacement in the Bitterroot National Forest in Montana and reported that 95% of the construction-related sediment occurred in the first 2 h after diversion removal. He further stated that sediment concentrations decreased to near pre-project levels within 24 h. He sampled stream sediment concentrations after the new culvert had been installed and the stream returned to its bed.

Allowable suspended sediment/turbidity standards for surface water quality are set individually by each state in the United States. Idaho state criterion for cold water aquatic habitat require that turbidity not exceed the background level by more than 50 NTU instantaneously or more than 25 NTU for more than 10 consecutive days (IDEQ, 1994). Other states are more stringent. Washington state criterion for Class AA (high priority) surface waters, which includes forested lands, requires that turbidity not exceed 5 NTU above the background level if the background turbidity is 50 NTU or less (WDE, 1997). California forested lands criterion vary by region from 1 NTU above background to 20% above background (Rosetta, 2005).

These criteria are intended to provide protection to cold water species. More specific criteria are available for selected species. Suspended sediment concentrations of 6000 mg/L for 1 h have caused avoidance behavior in coho salmon (Noggle, 1978). Concentrations of 500 mg/L for 3 h were observed to cause sublethal stress in adult steelhead (Redding and Shreck, 1982). Concentrations of 25 mg/L for 1 h resulted in decreased feeding rates in juvenile coho salmon (Noggle, 1978).

Road obliteration proceeds with the assumption that long-term benefits outweigh short-term effects on stream water quality. Measurements of in-stream sediment concentrations, especially during and immediately after excavations, would provide data to support or refute this assumption. The purpose of this study was to measure the effects of culvert removal on stream water quality. Stream flow and sediment concentrations were measured on multiple stream crossings for two national forests in Idaho and one in Washington. Specific objectives of this study were to:

1. Determine sediment concentrations during culvert removal;
2. Compare regulatory turbidity criteria to measured turbidity; and
3. Identify correlations between stream crossing characteristics and stream sediment concentrations and yields.

2. Methods

This study was not conducted in an experimental framework, but as an observational study. Skill and technique of the equipment operators, soil moisture, stream flow, and weather conditions were a few of the factors expected to have an impact on sediment concentrations and yields. Some of the locations were not independent because the culvert removal operations encountered crossings on streams that had upstream road obliteration a few days previous. The authors have chosen to use a significance level of 0.10 to account for this lack of experiment control. The results of this study should be considered an exploratory study.

2.1. Location descriptions

Horse Creek, located on the Nez Perce National Forest in Idaho, is a tributary to Meadow Creek in the Selway River drainage and is an important habitat for anadromous and resident fish. The Horse Creek drainage was an Administrative Research Study area from 1965 to 1988 when roads were constructed for a harvest operation. Stream flow and sediment concentrations were monitored year-round and sediment deposition was measured each year at dams constructed on multiple tributaries to Horse Creek (King, 1994). In 1998, monitoring stations, which had been discontinued in 1988, were restored on three streams in the Horse Creek drainage. Research and monitoring efforts have spanned a variety of successive activities including road installation, harvesting, and now road obliteration.

The Main Fork of Horse Creek has a drainage area of 1630 ha. The average annual precipitation ranges from 100 to 115 cm and the majority of runoff is spring snowmelt. Watershed elevations range from 1300 to 1700 m. Most hillside slopes range from 20% to 50%. The predominant geologic parent material is gneiss and schist derived from the Idaho Batholith Border Zone. Soils are moderately deep, well drained, loam to sandy loam with surface layers containing loessal silt. The dominant habitat type is western red cedar with subalpine fir and grand fir habitat types are also present (USDA Forest Service, 1981).

The Horse Creek drainage (Fig. 1) has a road density of 1.7 km/km². A 7.2-km mid-slope road was obliterated in 2003 and 2004. Three watersheds (H10, H14, and H16), 63, 58, and 24 ha in area, respectively, were monitored for this study. All three watersheds have similar southerly aspects and range in elevation from 1300 to 1700 m. The Rosgen channel type of each of the three streams is A4a+ (Rosgen and Silvey, 1998). All culverts removed from these streams

were 0.61-m (24 in) corrugated metal pipe (CMP). The fill volumes removed during road obliteration were 180, 890, and 220 m³ at H10, H14, and H16, respectively.

A second study area was located on the North Fork Granite Creek, a tributary to Priest Lake, on the Kaniksu National Forest in Washington. The North Fork Granite Creek has a drainage area of 7700 ha. Average annual precipitation ranges from 114 to 144 cm. Watershed elevations range from 1100 to 1400 m and hillslopes are typically 20–60%. The predominant geologic parent material is composed of glacial till and soils are heavily influenced by volcanic ash. Soils are shallow and poorly developed in some areas. The surface layers are mostly silt loam. The dominant habitat types surrounding Granite Creek are western red cedar and subalpine fir (USDA Forest Service, 2004).

The Granite Creek drainage (Fig. 2) has a road network with a density of 2.5 km/km². Periodic mass failures on unmaintained roads have resulted in increased sediment delivery to the North Fork Granite Creek that supports bull trout and westslope cutthroat trout. Maintenance of grizzly bear habitat is another ecological concern in the Granite Creek drainage. In 2005, the road network of 12.9 km was obliterated to reduce the risk of mass failures and to improve grizzly bear habitat. The removal of three culverts were monitored in the Granite Creek drainage: two on the North Fork Granite Creek, G1 and G2, and one on a tributary, G3. The Rosgen channel types are B4 for Granite Creek 1 and 2 and B5 for Granite Creek 3 (Rosgen and Silvey, 1998).

Unlike Horse Creek, these three monitored stream crossings were not all similar in size and aspect. Granite Creek had a larger drainage area and exhibited higher flows than the other study areas, but had lower gradients (Table 1). The drainage areas above G1 and G2 were 400 and 700 ha, respectively. The drainage area above G3 was

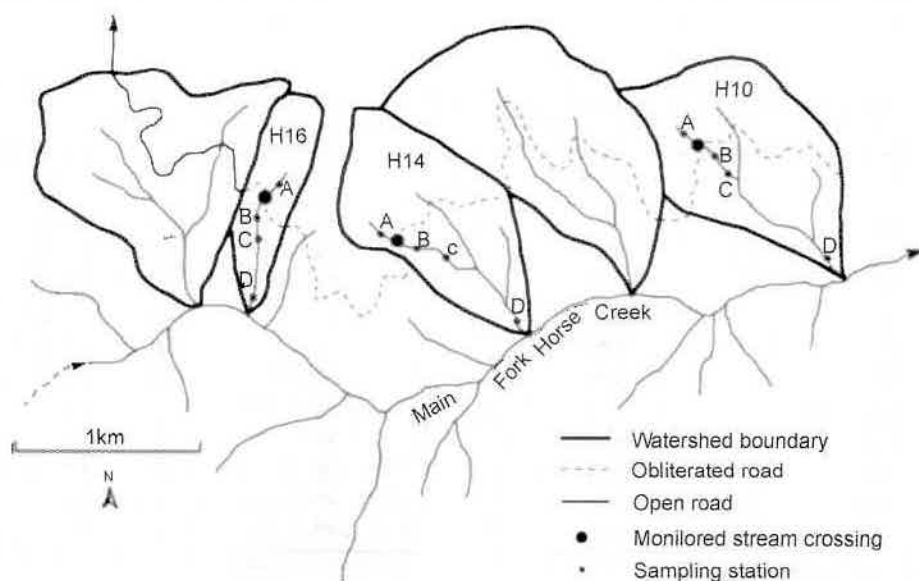


Fig. 1. Tributary watersheds and obliterated road network in the Horse Creek drainage of the Nez Perce National Forest, ID.

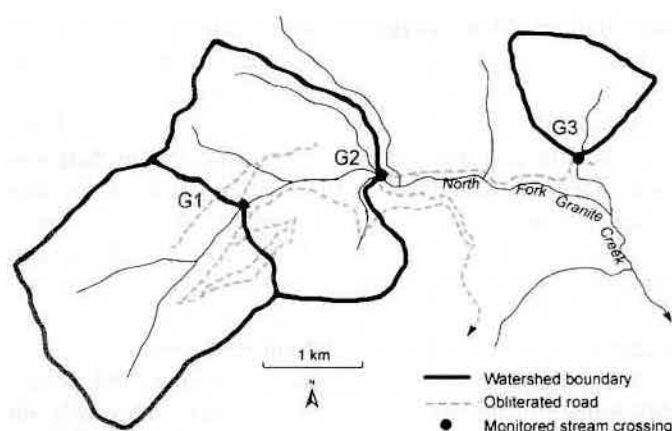


Fig. 2. Tributary watersheds and obliterated road network in the Granite Creek watershed of the Kaniksu National Forest, WA.

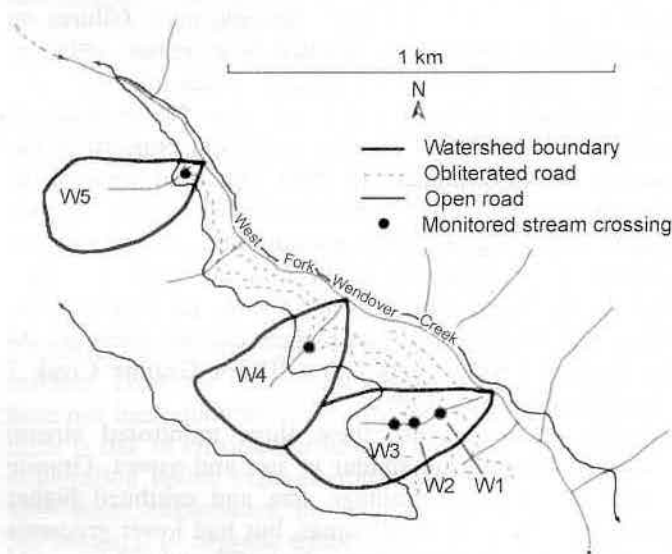


Fig. 3. Tributary watersheds and obliterated road network in the Wendover Creek drainage of the Clearwater National Forest, ID.

91 ha. Not all segments of the obliterated roads in Granite Creek were fully recontoured. Road segments with a lower risk of failure were partially recontoured. Road segments that were partially recontoured were ripped to a depth of 0.3–0.6 m and only the areas with fills judged to be unstable were recontoured. Culverts were removed and channel crossings were restored on all obliterated roads.

The third study area was Wendover Creek, a tributary to the Lochsa River, located on the Clearwater National Forest in Idaho on the western slopes of the Bitterroot Mountains. Wendover Creek is characterized by steep valley walls that have slopes of 60–90%. Average annual precipitation is 122 cm. The elevations of the monitoring locations ranged from 1130 to 1190 m. The parent material is granitic and surface soils are silt loam with weak granular structure. The dominant habitat type is western red cedar. The obliteration of five stream crossings (W1, W2, W3, W4, and W5) on three tributary streams to Wendover Creek were monitored. The drainage areas upslope of the stream crossings ranged between 16 and 19 ha (Brown, 2002).

Historically, Wendover Creek (Fig. 3) and the surrounding area were intensively logged, and had a higher road density (11.5 km/km²) than Horse Creek (1.7 km/km²) and Granite Creek (2.5 km/km²). The roads in Wendover Creek had log stream crossings rather than CMP culverts like Horse Creek and Granite Creek. Log stream crossings are constructed by placing logs in the stream and placing soil on top of the logs. Such crossings are known in California as Humboldt crossings and in Idaho as log culverts. This method was popular in the 1940s and 1950s but is not currently used.

2.2. Stream crossing characteristics

The three study areas exhibited a range of stream flow rates and watershed characteristics (Table 1). Flow rates

Table 1
Road crossing and stream characteristics on Horse Creek, Granite Creek, and Wendover Creek locations

Location	Stream crossing	Flow rate ^a (L/s)	Drainage area ^b (ha)	Gradient (m/m)	Stream power (W/m)	Culvert length (m)	Culvert type	Culvert diam. (m, inches)	Fill volume (m ³)
Horse Creek	H10	0.6	9.0	0.25	1.4	18	CMP	0.6, 24	305
	H14	0.1	3.4	0.42	0.53	24	CMP	0.6, 24	805
	H16	0.1	10.4	0.19	0.22	17	CMP	0.6, 24	200
Granite Creek	G1	13	400	0.05	6.0	15	CMP	1.5, 60	100
	G2	12	696	0.04	4.7	14	CMP	1.5, 60	350
	G3	9	91	0.10	8.8	12	CMP	0.9, 36	200
Wendover Creek	W1	0.4	19	0.28	1.0	23	Log	NA	460 ^c
	W2	0.4	19	0.32	1.1	28	Log	NA	380
	W3	0.4	19	0.34	1.2	22	Log	NA	460 ^c
	W4	0.4	19	0.29	1.0	15	Log	NA	460 ^c
	W5	0.4	16	0.23	0.90	14	Log	NA	460 ^c

^aAverage flow rate during road obliteration activity.

^bAs measured from stream crossing at obliterated road. This is the contributing area associated with monitoring station B.

^cThese values are not consistent with Brown (2002); however, the authors had greater confidence in these estimates.

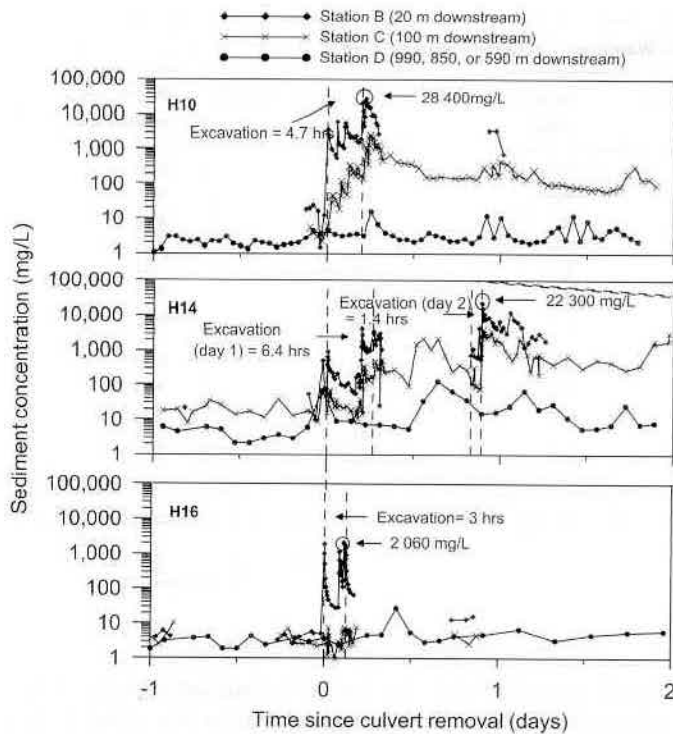


Fig. 4. Sediment concentrations at Horse Creek during culvert removal at 20, 100 m, and mouth of the drainages. Background concentrations at Horse Creek ranged from 5 to 13 mg/L. Dotted lines indicate beginning and end of excavation in stream bed.

were highest at the Granite Creek stream crossings, up to two orders of magnitude higher than flow rates at the Wendover and Horse Creek locations. The stream crossings at the Wendover and Horse Creek study locations were located on midslope roads, had smaller contributing areas, and steeper gradients. Stream power was greatest at the Granite Creek locations due to the larger stream flow rates even though they had the smallest stream gradients. The smaller stream gradients at Granite Creek required shorter culverts, which averaged 13 m in length while the culverts at Horse and Wendover Creeks both averaged 20 m in length. There were larger diameter culverts at Granite Creek.

2.3. Sampling

All obliteration activities took place during low stream flow in late summer. Sampling techniques were similar but not identical at each location.

Stream crossings at Horse Creek were sampled at four locations: A (5–15 m above the culvert inlet), B (20 m downstream from the culvert outlet), C (100 m downstream from the culvert outlet), and D (at the mouth of the tributary). The stations at D were located at distances of 990, 850, and 590 m downstream of the stream crossing at H10, H14, and H16, respectively. Stations A and C had permanent 2-in, 45° WSC trapezoidal flumes installed in 2000. WSC trapezoidal flumes were developed by Washington State College (now Washington State University)

for field irrigation use. Their ability to pass sediment and range of flow made them well suited for this application. Depth of water in the flume was recorded by a Campbell Scientific CR10X data logger every half hour. Water depths were converted to flow rates using the rating curve of the WSC flume. A temporary overflow that captured the entire stream was placed at station B for taking grab samples. Sampling at Horse Creek began at least one day prior to culvert removal and continued throughout the culvert removal activity. During culvert removal activities, grab samples were taken every 30 min in 500 mL bottles from flumes at the B and C locations and at the beginning and end of each day's work at the A station. Grab samples were taken from a free overfall, to ensure a well mixed sample. Additional grab samples were taken when excavator activity caused a visible change in sediment concentration, often as frequently as every 5 min. Samples were also taken with an ISCO 3700 sampler every hour at station D for the entire sampling period and at station C during the night.

Stream crossings at Granite Creek and Wendover Creek were sampled at two locations—one upstream and one downstream of the road crossing at distances approximating the "A" and "B" locations at Horse Creek. The samples at Granite Creek were taken with ISCO 3700 samplers and the samples at Wendover Creek were grab samples. Sampling began at least 8 h prior to culvert removal and continued throughout the culvert removal activity. Samples were taken every hour and when sediment concentrations changed visually because of excavator activity.

Turbidity and total sediment were determined using standard methods (American Public Health Association, 1998). Turbidity was determined using a Hach Model 2100N Turbidity Meter. All Horse Creek samples were analyzed for turbidity. At Wendover Creek a relationship between turbidity and concentration was developed (r -square = 0.84; mean square error = 0.132) from 227 randomly selected samples taken at all Wendover Creek locations. Turbidity was estimated for each sediment concentration sample at Wendover Creek using this relationship. Turbidity was not determined for Granite Creek samples.

2.4. Culvert removal methods

Culvert removal proceeded differently at Horse, Granite, and Wendover Creeks due to variations in management objectives, levels of oversight, operator techniques and stream crossing characteristics. Major differences among the three operations included log stream crossings versus CMP culverts, use of flow diversions, equipment contact with water, in-stream erosion mitigation, and stream structure additions (Table 2).

Wendover Creek had log stream crossings and stream diversion. Removal of log stream crossings was more difficult than removal of CMP culverts. It was difficult to

Table 2
Comparison of culvert removal techniques of Horse Creek, Granite Creek, and Wendover Creek locations

Location	Stream crossing	Culvert removal date/s	Flow diversion	Equipment in live water	In-stream erosion control ^a	Accumulated sediment ^b
Horse Creek	H10	10 Sept 03	No	No	Straw	Yes
	H14	24&25 Aug 04	No	No	Straw	No
	H16	29 Sept 04	No	No	Straw	Yes
Granite Creek	G1	10 Aug 05	No	Yes	No	ND
	G2	7 Sept 05	No	Yes	No	ND
	G3	14 Sept 05	No	Yes	No	ND
Wendover Creek	W1	25 Jul 01	No	Yes	No	ND
	W2	8 Aug 01	Yes	Yes	SB (1)	ND
	W3	14 Aug 01	Yes	Yes	SB (2)	ND
	W4	16&17 Aug 01	Yes	Yes	SB (2)	ND
	W5	22 Aug 01	Yes	Yes	SB (2)	ND

^aErosion control material placed in streambed before or during disturbance. Stream crossings at Wendover Creek had 0 or 2 sediment traps noted by straw bale (SB).

^bSediment accumulated at inlet of culvert.

separate soil from the logs of the log stream crossing before they were removed. The logs were often decayed, broke apart easily, and were extracted piecemeal by an excavator.

Stream flow at Wendover Creek was diverted at least one day prior to culvert removal. A metal dam with a 100 mm diameter flexible pipe was placed in the stream. The flexible pipe with the stream flowing inside was routed around the working area with the outlet placed downstream of any mitigation. The pipe had to be moved occasionally to prevent the excavator from running over it. No diversion was used at Horse Creek where the intent was to measure the unmitigated impact of culvert removals. No diversion was used at Granite Creek because the stream flow was too large.

Allowing the equipment to contact either water or the saturated stream bed was different among the locations (Table 2). The excavator operator at Horse Creek avoided traversing live water by planning excavator moves so that it was not necessary. At Wendover Creek the operator moved across either the water or saturated soils. At Granite Creek, the operator crossed the water many times to work on both sides of the crossing.

At every location, straw was spread in the stream crossing and on the recountoured road bed. At Wendover Creek, in-stream straw bales were used in various combinations among the five plots (Table 2). At all three locations, rocks were placed in the stream following culvert removal. Grass seed and additional straw were spread over the stream crossing within a few days following culvert removal.

2.5. Stream crossing characteristics and sediment response

Among the Horse, Granite, and Wendover Creek locations, culverts were removed at 11 stream crossings. The sediment response to culvert removal was analyzed and compared based on the physical characteristics of the

stream crossings. Sediment yield was calculated for each stream crossing for a 24-h period starting at the time of first impact ($t = 0$), which was approximately the time the first culvert section was removed.

A Spearman's Nonparametric Test (SAS, 2003) was conducted to identify correlations between ranked stream crossing characteristics and sediment responses. Stream crossing characteristics included flow rate, culvert length, drainage area, stream gradient, stream power, and fill volume. Stream responses were sediment yields and peak sediment concentrations. All of the stream response comparisons were based on samples taken 20 m downstream of the outlet of the former culvert (Station B).

3. Results

Eleven culvert removals were monitored. All but one, Horse Creek H14, were carried out during periods without rain. The rain at H14 during culvert removal resulted in a unique response, will be discussed separately, and was not included in statistical analysis. Of the 10 remaining locations, three (Wendover Creek W3, W4, and W5) had two straw bales in the stream. Where appropriate the effect of this mitigation will be noted.

3.1. Sediment concentrations

Sediment concentrations were measured at the outlet of the culvert for all ten locations and are shown in Figs. 4–6. The three Horse Creek locations also had sediment concentrations measured 100 and 900 m below the culvert outlets. Sediment concentrations above the culvert were unchanged by culvert removal and values were less than 10 mg/L.

At the culvert outlet for all ten locations there was an immediate response in sediment concentration beginning as soon as the first culvert section was removed ($t = 0$).

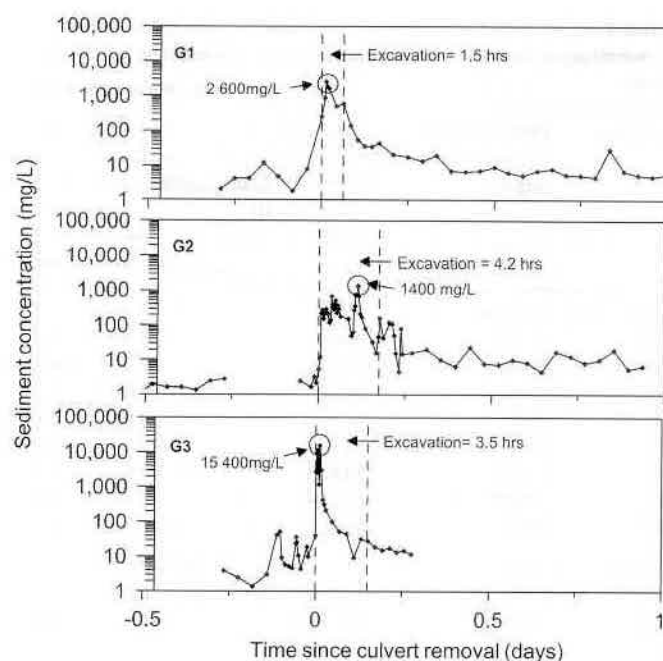


Fig. 5. Sediment concentrations at Granite Creek for station B (20 m downstream) during culvert removal. Background concentrations at Granite Creek ranged from 1 to 7 mg/L. Dotted lines indicate beginning and end of excavation in stream bed.

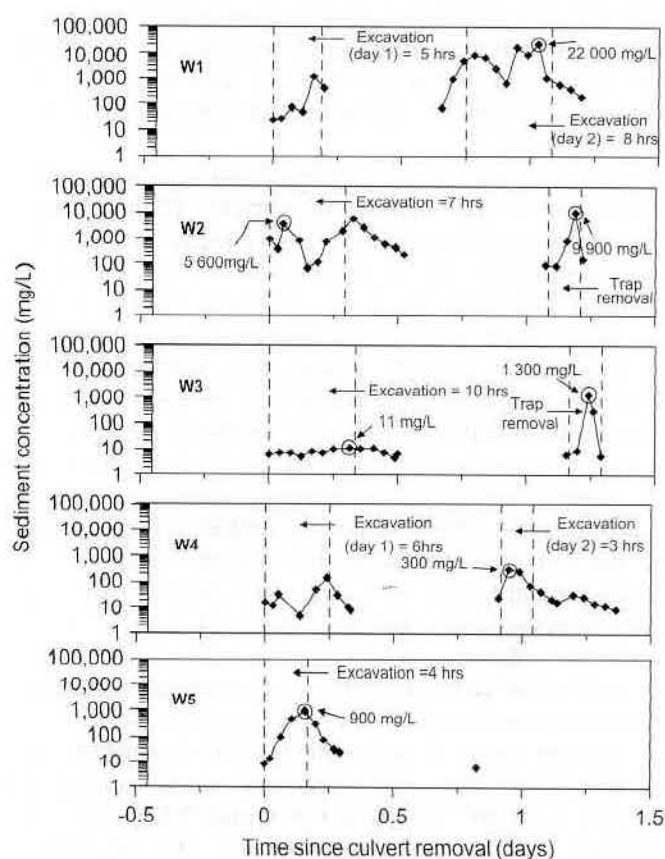


Fig. 6. Sediment concentrations at Wendover Creek for station B (20 m downstream) during culvert removal. Background concentrations at Wendover Creek ranged from 2 to 13 mg/L. Dotted lines indicate beginning and end of excavation in stream bed.

Removal of additional culvert sections, moving the excavator across the stream, or placement of rocks in the stream channel were the activities that caused the peaks in sediment concentration. The highest sediment concentration occurred during culvert removal activities, usually removal of the last culvert section, or within a half-hour after cessation of the days activity. Sediment concentration peaks for locations without mitigation ranged from 28,400 mg/L at H10 to 2060 mg/L at H16. The average for unmitigated locations was 13,000 mg/L. The range for mitigated locations was 900 at W5 to 11 mg/L at W3 with an average of 830 mg/L.

Sediment concentrations were measured 100 m below the culvert outlet at only three locations, all in Horse Creek. Peak sediment concentrations for these locations closely followed sediment concentrations at the culvert outlet, but were typically one order of magnitude less.

Sediment concentrations were measured at the mouth of the tributary, an average of 810 m downstream of the culvert outlet, for the same three Horse Creek locations. Sediment concentrations at these locations did not exceed sediment concentrations above the culvert, i.e., 10 mg/L. Dilution of the sediment from tributaries would decrease sediment concentrations. The tributaries had less flow than the main stream. Neither flows at the mouth nor the tributaries were measured which was an oversight and should be performed on future studies.

3.2. Sediment concentration and duration

The number of hours that sediment concentrations exceeded various cold water fish criteria are shown in Table 3. Three of the locations had sediment concentrations at the culvert outlet that exceeded 6000 mg/L for

Table 3

Duration of sediment concentrations exceeding various coldwater habitat criteria at 20 m downstream (B), 100 m downstream (C), and at the mouth of the stream (D)

Station	Location	Hours exceeding		
		6000 mg/L	500 mg/L	25 mg/L
B	H10	1.7	>10	>10.5
B	H14	3.4	>14	>14
B	H16	0	1.3	>3.1
B	G1	0	1.5	6.0
B	G2	0	0.9	5.5
B	G3	0.4	0.5	3.8
B	W1	4.3	12.9	>18
B	W2	0.5	11.7	>17
B	W3	0	0.6	1.7
B	W4	0	0	10.3
B	W5	0	1.7	6.3
C	H10	0	5	>47
C	H14	0	>18	>30
C	H16	0	0	0
D	H10	0	0	0
D	H14	0	0	10
D	H16	0	0	0.5

more than 1 h (the juvenile coho salmon avoidance criterion). These locations had no mitigation. At 100 m below the culvert (C station), none of the locations exceeded the juvenile coho salmon avoidance criterion. Similarly, at the mouth of the three streams that were monitored for sediment an average of 810 m downstream, this criterion was not exceeded. The sublethal stress criteria of 500 mg/L for 3 h was exceeded immediately below the culvert outlet at four of the 11 locations. Each of these locations had no mitigation. This criterion was exceeded at two of the three locations 100 m downstream and was never exceeded an average of 810 m downstream. The criterion for decreased feeding in juvenile coho salmon of 25 mg/L for 1 h was always exceeded at the outlet of the culvert, always exceeded 100 m downstream, and was exceeded at one of three locations 850 m downstream. Mitigation did not prevent exceeding the juvenile coho salmon feeding criterion.

3.3. Turbidity and regulatory compliance

Only Horse Creek and Wendover Creek, for a total of seven locations, had turbidity data to compare to Idaho regulatory compliance. All locations exceeded the Idaho allowable turbidity level for the instantaneous criterion (50 NTU above background) immediately below the culvert outlet. Peak turbidity values ranged from nearly 27,000 to 620 NTU. One hundred metre below the culvert outlet two of the three Horse Creek locations (H10 and H14) exceeded the instantaneous criteria. At the tributary mouths, an average of 810 m below the culvert outlet, none of the Horse Creek locations exceeded the instantaneous turbidity criteria. Moving 100 m downstream was not sufficient to meet the instantaneous criteria. However, moving an average of 810 m downstream was sufficient as long as rain sufficient to produce runoff from the bare road did not occur.

3.4. Sediment yields

Sediment yields based on a 24-h monitoring period at the culvert outlet were used to compare sediment delivery from each location (Table 4). Unbalanced ANOVA results indicated there was a statistically significant difference (p -value of 0.079) in sediment yield between the mitigated and the unmitigated locations. The range of sediment yield for the unmitigated locations was 170 kg (H10) to 2.6 kg (H16) with an average of 67 kg. The range for the mitigated locations was 3.1 kg to 0.2 kg, all at Wendover Creek. The average mitigated location sediment production was 1.6 kg.

3.5. Stream crossing characteristics and sediment response

Four stream crossings were not monitored for 24 h following the initiation of culvert removal because the water at the stream crossing appeared to have returned to pre-work sediment concentrations. For these four locations

Table 4

Concentration, turbidity, and sediment yields immediately below culvert outlet

Location	Peak sediment concentration (mg/L)	Instantaneous peak turbidity at station B (20 m downstream) (NTU)	24-h Sediment yield	
			(kg)	(m ³)
<i>Unmitigated locations</i>				
H10	28 400	26 890	171.0	0.21
H14	22 300	25 758	19.2	0.024
H16	2100	2527	2.6	0.033
G1	2600	ND ^a	98.6	0.12
G2	1400	ND ^a	49.2	0.062
G3	15 400	ND ^a	99.0	0.12
W1	22 000	> 1000 ^b	70.4	0.088
W2	9900	> 1000 ^b	25.5	0.032
<i>Mitigated locations</i>				
W3	1300	> 1000 ^b	0.2	0.003
W4	300	616	1.4	0.018
W5	900	> 1000 ^b	3.1	0.039

^aTurbidity was not measured at Granite Creek stream crossings.

^bSediment concentration relationship determined from Wendover Creek samples could not be applied to samples exceeding 1000 NTU.

(H16, G2, G3, and W5), sediment concentration values for the 1–17 h from the end of sampling to the full 24-h period were estimated based on the last measured sediment concentration values. All estimated concentrations were less than 16 mg/L.

The stream characteristics considered were stream flow and volume of the fill above the culvert. All other stream characteristics listed in Table 1 were highly correlated to each other with p -values less than 0.10. The culvert removal sediment responses were 24-h sediment yield, 1-h peak sediment concentration, peak sediment concentration, and the duration of turbidity values above background. One hour peak sediment concentration was the highest sediment concentration that occurred in the first hour after initiation of culvert removal. The peak sediment concentration was the highest sediment concentration during the culvert removal period. The exceedence duration corresponded to the number of hours the turbidity levels were above the Idaho standard for cold water aquatic habitat (50 NTU above background). Because there was a statistically significant difference between mitigated and unmitigated locations, the two were analyzed separately. The only significant correlations between stream characteristics and the culvert removal sediment responses were between stream flow and 24-h sediment yield (correlation coefficient = 0.69; p -value = 0.06) and fill volume and duration of turbidity values above the background (correlation coefficient = 0.90; p -value = 0.04). Stream flow explained 48% of the variation in the 24-h sediment yield. As stream flow increased, so did 24-h sediment yield. Higher flows eroded more material. The fill volume at the

stream crossing explained 81% of the duration of turbidity values above the background. Larger fills resulted in a longer duration above the turbidity thresholds.

3.6. Culvert removal and storm events

The culvert removal in watershed H14 at Horse Creek was carried out during a period of five consecutive days of rain that totaled 77 mm and provided a unique opportunity to observe the impact of rain on sediment yield during culvert removal on sediment yield. During the night of August 24–25 and the day of August 25 (time since culvert removal of 8–26 h), there were three periods of rain that totaled 60 mm (Fig. 7). The first storm began 8 h after the removal of the first culvert section. The storm lasted 2 h, produced 5 mm of rain with a peak 30-min intensity of 5 mm/h. It was followed half an hour later by a storm that lasted 5 1/2 h, produced 35 mm of rain with two peak 30-min intensities of 15 and 14 mm/h. This storm was the 7th largest in the 44-month period that rainfall was recorded (October 2001–June 2005). The final storm began 4 h after the second one, lasted 8 h, produced 12 mm of rain with a peak 30-minute intensity of 9 mm/h.

Prior to the first storm at the end of the work day on August 24, all sections of the culvert were removed and the stream banks were reshaped. The road had been reshaped on one side of the stream crossing. On the side of the stream crossing where the equipment was working, the road was ripped but not reshaped. No straw was placed on either side of the stream crossing. These activities left a strip of bare soil 134 m long and 10 m wide, the former road, that could contribute runoff and sediment to the stream and two shorter strips 10 m wide and 10 m long, where the fill had been removed, immediately adjacent to the stream.

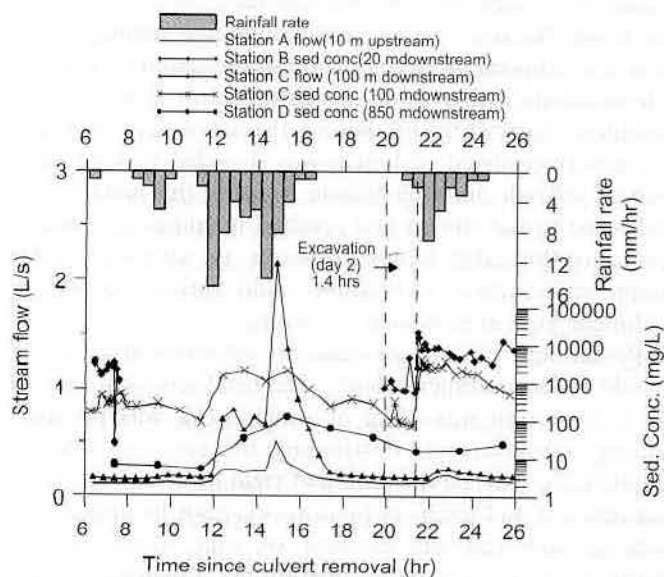


Fig. 7. Rainfall, runoff, and sediment concentration at location H14 during a storm.

The first storm did not change stream flow 26 m above the road (station A) nor 100 m below the former culvert outlet (station C). Sediment concentrations remained unchanged at station C and at the stream mouth 850 m downstream (station D). The former road prism that was disturbed infiltrated the first storm, which implies an infiltration capacity of at least 5 mm/h.

During the second storm, stream flows at station A increased from 0.3 to 0.5 L/s. This increase in stream flow of 66% reflected the response of the undisturbed forest to the storm. Stream flows at station C increased from 0.3 L/s to a peak of 2.2 L/s. This increase in stream flow of 630% reflected the contribution of the 134 m long strip of bare, disturbed road section and an additional 4000 m² of forest floor, the additional contributing area between the former road and the C station. The stream returned to its pre-storm flow rate two hours after the cessation of rainfall at the A and C stations. Sediment concentrations at station C increased by an order of magnitude from 100 to 2000 mg/L in response to the second storm. The storm related sediment concentrations were an order of magnitude larger than during culvert removal the previous day (Fig. 4). Sediment concentrations at C were near pre-storm concentrations 2 h later, similar to the A station. At the stream mouth, the sediment concentration peaked by an order of magnitude and was elevated for at least 10 h until the start of the third storm. The former road prism that was disturbed was not able to infiltrate the second storm, which implies an infiltration rate of less than 15 mm/h.

Culvert removal began again the morning of August 25 between the second and third storms, continued for 1.4 h, and ceased just prior to the third storm. The increases in stream flow at the A and C stations from the third storm were minor compared to the stream flow increases from the second storm. Stream flow at the A station increased from 0.14 to 0.20 L/s, a 43% increase. At the C station stream flow increased from 0.17 to 0.26 L/s, a 53% increase.

Sediment concentrations at the culvert outlet reached the highest value caused by excavation activity, a value of 8100 mg/L, immediately prior to the start of the third storm. During the third storm, but in the absence of culvert removal activities, the sediment concentrations reached a maximum of 22 300 mg/L for this crossing. Unlike the other locations, the highest sediment concentration was not during culvert removal activities, but during rain.

Sediment concentration at station C increased from 100 to 4000 mg/L and remained above 1000 mg/L for over 2 h. This increase in sediment concentration was due to the strips of bare soil adjacent to the stream crossing.

3.7. Road construction and culvert installation versus culvert removal

The construction of the road and installation of culverts at Horse Creek was monitored in 1978 and 1979. Sediment generated from road pioneering and building activities was

Table 5
Comparison of sediment yields from culvert installation and culvert removal.

Location	Monitoring time (hr)	Average stream flow rate (L/s)	Sediment yield (kg)		
			Station A	Station B	Station C
<i>Removal</i>					
H10	25	0.6	0.31	170	19
H14	30	0.1	0.23	33	10
H16	21	0.1	0.10	2.23	0.05
<i>Construction^a</i>					
H14 (I)	26	0.6	0.13	12.8	84.1
H16 (I)	12.2	1.1	0.86	9.3	ND
H14 (P)	23	1.1	0.30	ND	96.7

^aUSDA (1981) Pioneering (P) and culvert installation (I).

monitored in watersheds H14 and H16 (USDA, 1981). More sediment reached station C during road pioneering and culvert installation work at H14 and H16 than from the culvert removal operations (Table 5).

4. Discussion

Road obliteration and the associated culvert removals often proceed under the assumption that long-term benefits outweigh short-term consequences. During a 25-year return period rain-on-snow event on the Clearwater National Forest, there were 526 landslide events that occurred on roads similar to those obliterated at Wendover Creek and Horse Creek (McClelland et al., 1999). Their data implied an average of 400 000 kg of sediment were delivered to the stream from each road related landslide. Short term impacts of culvert removals reported in the present study were sediment yields from culvert removals without mitigation ranging from 170 to 2.6 kg. Idaho turbidity and salmon tolerance sediment concentration requirements were exceeded in the stream where the work was conducted but not an average of 810 m downstream. This comparison suggests that sediment loss from culverts is small and short lived and eliminates the risk of culvert plugging and failure.

At Horse Creek much of the sediment yield was observed to come from sand sized material placed for culvert bedding when the culvert was installed. As each culvert section was removed this material formed a cast of the outside of the culvert and became the bed of the stream. Over the course of a day the stream transported this material. Placement of rocks in the stream bed caused transport of the bedding material. The authors observed more scour of this material than bank caving. At Granite Creek there was no bedding material. Most of the sediment was observed to come from the stream bed as it adjusted to the bare soil and recently placed rocks. At Wendover Creek most of the sediment was observed to originate from the stream bed.

The authors observed several 150 mm by 150 mm by 25 mm depositions behind logs at Horse Creek between the B and C stations. There were few such deposits below the C station. A year after the culvert removals the authors did not observe these deposits. At Willow Creek fine material was observed coating rocks in the pool below the culverts, but not a year later.

Horse Creek H10 had elevated sediment concentrations and the highest sediment yield. Sediment had deposited at the culvert inlet for 25 years since the installation of the culvert. When the most upstream section of culvert was removed, the stream began to erode the accumulated sediment and did so for several hours. The authors suggest that this accumulated sediment contributed to the high sediment concentrations and yield. Removal of this sediment might have reduced the duration of the high turbidity and the sediment concentrations.

All of the stream crossings at Wendover Creek were constructed of logs rather than metal pipes. Although the study contained log and metal culvert locations, a comparison between the two was confounded by diversion and mitigation. All Wendover locations had stream diversion. This was physically possible at Horse Creek, but not at Granite Creek due to the higher flows. Comparison of the removal of log stream crossings with stream diversion to the removal of CMP without diversion suggests that sediment yields were consistent among all three locations. Without stream diversion, flows would access loose sediment around the log stream crossings and have increased sediment concentrations and yields, which suggests that stream diversion when log stream crossings are removed is necessary to allow them to have similar sediment yields as the removal of CMP.

Wendover Creek, W3, W4, and W5, were the only locations with mitigation using two straw bales. These mitigation measures were sufficient to reduce the peak sediment concentrations and turbidity as well as their duration. Because of these reductions, the sediment yield was also reduced. A large portion of the sediment yields at the locations with erosion mitigation came from cleaning sediment traps (Fig. 6). Before the straw bale sediment traps were removed, sediment was shoveled by hand from behind the bale onto the hillside. Some of this material was delivered to the stream and resulted in spikes of sediment concentration and minor increases in sediment yields. Improved cleaning techniques could further reduce the sediment load at mitigated locations.

Postponing the culvert removal activities after storms would reduce sediment yields. The total sediment yield at H14, C station was 33 kg of which 11 kg was produced during a rain storm. Postponing the removal activities would have reduced the sediment yield by one-third. While the amount and intensity of storms cannot be anticipated, wet ground and the amount of rain would provide justification to postpone operations. Ensuring ground cover on fresh soil at the end of each day and prior to anticipated rainfall would reduce sediment yield.

This study does not replicate Jakober's conclusion that 95% of construction-related sediment occurs in the first 2 h following diversion removal (Jakober, 2002). At Horse Creek locations where flows were low and sediment concentrations were elevated for several hours after culvert removal, less than 15% of the sediment yield was attained in 2 h. To achieve 95% of the culvert related sediment required 23 h. At the Granite Creek locations where flows were higher, 40–95% of the sediment was attained in 2 h.

5. Conclusions

Culvert removals during road obliteration operations were monitored at 11 locations on national forest lands in Idaho and Washington. Sediment concentration and turbidity were measured for a day prior to removal, during removal, and for at least a day afterwards. Based on this study, a similar culvert removal operation without in-stream mitigation would be expected to (1) have a peak sediment concentration between 28 400 and 2060 mg/L with an expected value of 13 000 mg/L, (2) have a sediment yield of between 170 and 3 kg with an expected value of 67 kg, and (3) exceed the Idaho instantaneous cold water turbidity criterion at the culvert outlet, but not an average of 810 m downstream. For a location with two in-stream straw bales the expectations would be to (1) have a peak sediment concentration of between 1300 and 300 mg/L with an expected value of 830 mg/L, (2) have a sediment yield of between 3 and 0.2 kg with an expected value of 1.6 kg, and (3) exceed the Idaho instantaneous cold water turbidity criteria at the culvert outlet, but not an average of 810 m downstream. Sediment yield from culvert removal was less than from road pioneering and culvert installation.

Sediment concentrations and turbidity dropped with distance from the culvert outlet. Moving 100 m downstream, sediment concentrations were one order of magnitude less than at the culvert outlet and exceeded the Idaho instantaneous turbidity criterion at two of the three locations. Moving 810 m downstream, sediment concentrations returned to near background levels and none of the three locations exceeded the instantaneous turbidity criteria. Only where a storm increased runoff and flushed sediment to the stream mouth was it possible to discern that culvert removal occurred an average of 810 m upstream.

Sediment concentrations also dropped with time. At the culvert outlet only three of the 11 locations (27%) had sediment concentrations that exceeded 6000 mg/L for more than 1 h. Four of the 11 locations (36%) had sediment concentrations that exceeded 500 mg/L for 3 h.

Mitigation consisting of stream diversion and two in-stream straw bales resulted in a statistically significant difference in sediment yield. This level of mitigation is recommended. Mitigation is necessary to keep sediment concentrations from log stream crossing removals comparable to CMP removals.

A series of rainstorms with a total rainfall of 60 mm exacerbated sediment concentrations and sediment yield

compared to culvert removal alone. While the impacts of the storm could have been reduced by placement of erosion control material and ceasing operations, neither the sediment concentrations nor yield was inconsistent with other locations in the study. When soils are wet and storms are forecast, extra erosion control material should be placed on the bare soil adjacent to the culvert removal location.

This study is a portion of an on-going assessment of road obliteration impacts. At Horse Creek, one of the primary impacts of roads was increased sediment yields that remained above pre-disturbance levels eight years after road construction. Currently, efforts are underway to determine recent sediment transport between the Horse Creek tributaries of this study and 3–6 km downstream at the confluence of the Main Fork and the East Fork Horse Creek. These data will help to predict whether culvert removals associated with road obliteration will allow streams to return to their pre-development sediment loads. Long-term stream flow rates and sediment deposition measurements will help to identify bedload transport rates and the amount of time required for stream recovery following culvert removals. This information will allow insight on the potential of restoration to return logged and roaded watersheds to pre-road conditions.

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Anthropogenic N₂O production from landfill leachate treatment

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Abstract

The results of a field survey and laboratory study indicated that nitrogenous landfill leachate treatment can be a significant potential source of N₂O emission. Nil (raw leachate) to 58.8 ng mL⁻¹ h⁻¹ (sequential batch reactor) N₂O emission was detected at five treatment plants in South China. The production and emission of N₂O was especially high soon after the raw leachate was aerated. The emission was positively correlated with the dissolved N₂O content in leachate; detected dissolved N₂O ranged from 0 to 1309 ng mL⁻¹. All leachate treatment plants studied were effective in NH₄⁺-N removal (>95%); however, the highest N₂O emission was estimated to be 0.25 g N₂O capita⁻¹ year⁻¹, comparable with the rate of N₂O emission in conventional sewage treatment process.

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Keywords: Nitrous oxide; Landfill leachate; Treatment; Greenhouse gas.

1. Introduction

Landfill is an important method for municipal solid waste (MSW) disposal (Cho et al., 2002; USEPA, 2003; Zouboulis et al., 2001). Leachate is formed as an unavoidable by-product of landfill operation. It contains a variety of inorganic and organic matters (Bernard et al., 1997; Chu et al., 1994; Lo, 1996), of which ammoniacal nitrogen (NH₄⁺-N), a product of biological degradation of nitrogenous organic matter, is a major constituent. The mean NH₄⁺-N concentration of landfill leachate in the UK is 900 mg L⁻¹, while higher NH₄⁺-N concentrations from 2000 to 5000 mg L⁻¹ have been reported in China (Lee et al., 2002; Robinson, 1991). To prevent environmental contamination, landfill leachate should be properly treated before discharge. The removal of NH₄⁺-N in leachate is one of the major tasks of the treatment (Heavey, 2003). Various physicochemical and biological techniques have been used

in leachate treatment, such as ammonium stripping (Calli et al., 2005; Cheung et al., 1997), activated carbon adsorption (Fettig et al., 1996; Imai et al., 1995; Kurniawan et al., 2005a), ozonation (Kurniawan et al., 2005b) and membrane filtration (Kurniawan et al. 2006; Peters, 1998). Among these, ammonia stripping and biological processes which involved nitrifiers and denitrifiers are most commonly used (Britz et al., 1990; Ho et al., 1974; Robinson and Maris, 1985; Wong et al., 1990). In the main-stream processes, nitrification converts NH₄⁺-N to NO₂⁻ and NO₃⁻ under oxic conditions, and denitrification converts NO₃⁻ to N₂O and N₂ under anoxic conditions. However, nitrous oxide (N₂O) is a common by-product of nitrification and denitrification and is also produced through other compound-nitrogen degradation processes such as anammox, heterotrophic nitrification and nitrifier denitrification (Laursen and Seitzinger, 2002; Schmidt et al., 2003). Landfill leachate contaminated materials, e.g., saw dust, may also release a significant quantity of N₂O (Hui et al., 2003).

N₂O is an important trace gas that causes undesirable environmental problems such as greenhouse effect and ozone depletion in the stratosphere. N₂O has a (100-year)

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296-fold global warming potential compared to CO₂. The concentration of atmosphere N₂O is estimated to be about 8% higher than the value in the pre-industrial era, and it is increasing by 0.2–0.3% per year (ICPP, 2001). Anthropogenic activities have been determined to be the significant source of N₂O emission (Khalil and Ramussen, 1992), of which more than half results from microbial activity (Davidson, 1991).

Waste treatment processes might be significant sources of anthropogenic N₂O emission. Garrido et al. (1997) reported 2 kg N₂O-Nm⁻³d⁻¹ production from nitrifying biofilms. Gejlshjerg et al. (1998) conducted a semicontinuous and batch laboratory scale experiments with activated sludge from a Danish wastewater treatment plant. The results indicated that most of the N₂O emission occurred under oxic conditions, suggesting a coupling between NH₄⁺ oxidation and NO₂⁻ reduction (nitrifier-denitrification) being responsible for the majority of N₂O production. The results of Itokawa et al. (2001) indicated that 20–30% of influent nitrogen could be emitted as N₂O in laboratory-scale bioreactors of intermittent aeration supplied with high-strength wastewater with a low influent COD/N ratio of less than 3.5. Park et al. (2000), using a lab-scale intermittent aeration reactor fed with domestic wastewater, reported high N₂O emission in the beginning of the aerobic phase rather than the anoxic phase. Su et al. (2003) estimated that 0.002 and 0.011 kg N₂O head⁻¹ year⁻¹ was emitted through anaerobic treatment in livestock wastewater of Taiwan. Hobson et al. (2005) reported that N₂O emission in vermicomposting was mostly due to the low oxygen pressure in the intestine of the worm.

Although reports are readily available indicating that landfill cover and leachate contaminated water are possible significant source of N₂O (Bogner et al., 1999; Lee et al., 2002), N₂O production from landfill leachate treatment work is not yet recognized as a significant source for the global budget (Oonk, 1996). The aim of this study was to quantify the N₂O emission rate, the dissolved N₂O concentration and their relationship with nitrogen budget under conventional landfill leachate treatment conditions.

2. Materials and methods

2.1. Landfill site

Five MSW landfill sites in the Pearl River Delta of Guangdong Province, China, were chosen for the present field survey and laboratory study (Table 1).

2.1.1. Datianshan landfill

It is located in the east suburb of Guangzhou, the capital city of the Guangdong Province. It operated from 1989 to 2003. Impermeable bottom and top liners had been provisioned. Field sampling for leachate samples was conducted in April 2004. Five types of samples were collected, representing different phases of the treatment process: discharge pipe of raw leachate (R), temporary storage pond (SP), primary biological treatment tank (BT1) (aerated, retention time was 24 h), secondary biological treatment (BT2) (extended aeration for another 24 h) and effluent (E) (discharge to a nearby stream) (Table 2).

2.1.2. Likeng landfill

Likeng landfill is located in the north of Guangzhou, operated from February 1992 to December 2003. Landfill area was 0.34 km². Impermeable top liners were installed only after the site closure. It was a recirculating landfill (Benson et al., 2007); leachate recirculation was practiced since it begun to accept MSW (Lee et al., 2002). Leachate was treated by an *in situ* leachate treatment plant. Field sampling was conducted in July 2004. Seven types of leachate samples were collected: raw leachate (R); primary aeration tank (PA) (to increase the dissolved oxygen (DO) level in leachate); primary sedimentation tank (PS) (mixed with lime for NH₃ stripping); biological aeration tank (BA1) treatment; secondary aeration tank (BA2); chemical treatment (CT) tank and secondary sedimentation tank (SS) before discharge.

2.1.3. Shuikukeng landfill

It is an on-going site, operated since May 2001 in Zhongshan City. Raw leachate (R) is directed to a storage pond (SP) for temporary storage. In the treatment process, leachate is firstly mixed with lime and sprayed (Str) for the purpose of NH₃ stripping. Then, the leachate pH is adjusted to neutral and pumped to the aeration tanks (A). Partially treated leachate is passed to the oxidation ditch (OD) for further biological (aerobic) treatment. Finally, effluent (ODE) is transferred into a tank (E) for temporary storage before discharge. The overall retention time for all of the treatment processes is 24 h. Leachate samples were collected in November 2004.

2.1.4. Guoqiaowo landfill

Guoqiaowo landfill is located in Bao-an District of Shenzhen City. It begun to accept MSW in 1993. It was an open dumping site with minimal engineering control.

Table 1
Capacity of MSW loading and leachate production rates in the five landfills

	Datianshan	Likeng	Shuikukeng	Guoqiaowo	Xiaping
Annual MSW loading (t)	700,000	550,000	290,000	80,000	700,000
Capacity of MSW loading (t)	4,120,000	9,000,000	1,500,000	800,000	46,930,000
Leachate production rate (m ³ d ⁻¹)	500	410	400	50–80	400–800
Leachate treatment capacity (m ³ d ⁻¹)	500	400	350	50	800

Table 2
Physicochemical properties of landfill leachate samples

Landfill	Treatment	Physico-chemical properties				
		Temperature (°C)	pH	DO (mg L ⁻¹)	COD _{Cr} (mg L ⁻¹)	BOD ₅ (mg O ₂ L ⁻¹)
Datianshan	Raw leachate	37.0	8.77	ND	16,190	4102
	Storage pond	23.5	8.62	ND	5760	3802
	Biological treatment 1	23.0	7.99	1.5	5540	1402
	Biological treatment 2	23.4	8.73	8.0	890	202
	Effluent	23.8	8.50	2.9	509	122
Likeng	Raw leachate	30.0	8.47	ND	3120	2600
	Primary aeration tank	31.2	8.58	0.6	5020	5900
	Primary sedimentation tank	31.0	8.51	ND	3520	2350
	Biological aeration tank 1	31.2	8.42	5.4	280	1050
	Biological aeration tank 2	32.0	8.50	4.9	260	270
	Chemical treatment	29.4	9.29	4.2	214	240
	Secondary sedimentation tank	29.6	9.95	0.8	190	130
Shuikukeng	Raw leachate	34.5	8.66	ND	11,140	7300
	Storage pond	24.3	8.66	ND	9610	6100
	Ammonia stripping	29.0	9.48	ND	5670	3200
	Aeration tank	23.3	7.13	5.0	4370	2800
	Oxidation ditch	24.0	6.99	5.7	3820	1350
	Oxidation ditch effluent	24.0	6.80	1.7	1650	1400
	Effluent	21.4	7.90	3.3	1329	1425
Guoqiaowo	Raw leachate	25.6	8.61	1.4	17,020	4300
	Storage pond	19.6	8.60	ND	14,090	4300
	Ammonia stripping	20.2	11.31	3.1	9280	2450
	Anaerobic tank	23.0	8.33	ND	5020	1450
	Aeration tank	24.0	7.43	1.8	4480	1350
	Ozone treatment tank	22.0	6.94	8.0	3400	1125
	Secondary aeration tank	22.0	7.13	4.8	3140	1300
	Effluent	21.8	6.85	4.3	1105	1050
Xiaping	Raw leachate	31.0	8.12	1.7	20,680	6100
	Storage pond	28.0	8.08	ND	18,060	5600
	Ammonia stripping	20.0	9.85	ND	15,340	3750
	Anaerobic tank	21.0	7.95	ND	5390	2050
	Sequencing batch reactor (SBR)	25.2	7.42	2.2	760	435
	Effluent	22.2	8.06	2.8	387	375

ND: not detected.

To safe guide the water quality of a nearby Shiyan Reservoir, an *in situ* leachate treatment plant was built and the operation commenced in May 2004, soon after the site closure. Raw leachate (R) was collected and temporary stored in a storage pond (SP). Lime was added and sprayed for ammonia stripping (Str). After pH was adjusted to about 7, a 3–4 day anaerobic treatment (An) was followed. Then, the leachate was transferred to an aeration tank (A). Ozone treatment (Ozone) was conducted before passing to the secondary aeration tank (SA) for biological (aerobic) treatment. The retention times of the overall aeration and ozone treatment process was 24 h. Field sampling was conducted in December 2004.

2.1.5. Xiaping landfill

Xiaping landfill was designed as a dry bioreactor and expected to serve the Shenzhen City for 30 years. It is located in the near suburb of Shenzhen and has been in

operation since October 1997. Bottom liner and different types of permanent and temporary top liners had been installed to minimize leachate generation. Leachate was treated by an *in situ* leachate treatment plant before being discharged and mixed with domestic sewage for further treatment. Raw leachate (R) was temporary stored in a storage pond (SP). Then, lime was added for ammonia stripping (Str) in two stripping towers. The pH was re-adjusted to about 7 before anaerobic treatment (An). There was a sequential batch reactor (SBR) treatment for 24 h before being discharged as effluent (E). Field sampling was conducted in December 2004.

2.2. Physicochemical parameters

DO in the leachate samples was determined *in situ* using a portable DO meter (Shanghai Precise Scientific Apparatus Co. Model JPB-607). Leachate temperature was

measured by using a glass thermometer. Field samples were collected and chilled before laboratory measurement. The pH was determined using a Sartorius PB-10 pH meter. The BOD₅ was determined according to a standard method (APHA, 1995). HACH COD Reactor and DR890 Colorimeter were used for COD_{Cr} analysis, respectively. K₂S₂O₈ oxidation and UV spectrophotometry were used for total nitrogen (TN) determination. Titrimetric method was used for the determination of NH₄⁺-N levels, while Devarda's alloy reduction method was used for NO₃⁻-N analysis (APHA, 1995).

Dissolved N₂O concentration in the leachate was determined according to Barnes and Owens (1999). For a 60-mL glass syringe, 25 mL was filled with leachate, leaving a 25-mL headspace with ambient air. It was then shaken vigorously for 10 min. The volume expanded in the headspace was recorded and gas sample in the headspace was collected by a pre-evacuated gas sample tube (Isochem) for N₂O quantification (Lee et al., 2002). The concentration (ng mL⁻¹) of dissolved N₂O in leachate was calculated as

$$\text{Dissolved N}_2\text{O in leachate (ng mL}^{-1}\text{)} = [(A + B) \times C - D] / A,$$

where A = leachate volume collected by syringe (mL); B = gas expansion (mL) in the headspace; C = N₂O concentration calculated from a standard curve (ng mL⁻¹); D = extracted-air volume $\times$ N₂O concentration in ambient air (ng mL⁻¹).

The quantity of 24-h N₂O emission was determined by collecting 15 mL of leachate sample in a 30-mL syringe with the headspace filled with ambient air. The syringes were then incubated at room temperature of 23–25 °C for 24 h. Gas sample in the headspace was then collected by a pre-evacuated gas sample tube for N₂O quantification. N₂O determination was quantified using a HP4890 Gas Chromatography with a Porapak Q stainless-steel column (80/100 mesh; 35 cm in length $\times$ 1/8" internal diameter) as described by Lee et al. (2002). Nitrogen was used as the carrier gas (15 mL min⁻¹). Other operation conditions included: injector (110 °C); detector (ECD) 350 °C; oven 70 °C; retention time: 7 min per sample. One ppm N₂O standard gas in N₂ (Alltech 73068) and ambient air was used for calibration (N₂O in air was assumed to be 315 ppbv or 0.575 ng mL⁻¹). Results were analyzed using software ChemStation provided by HP. 24-h N₂O flux (mass) was quantified as

$$\text{N}_2\text{O (ng mL}^{-1}\text{ leachate h}^{-1}\text{)} = (N - M) / V_1 / V_2 / 24,$$

where N , concentration of N₂O in headspace after 24 h; M = N₂O concentration of ambient air; V_1 , volume of head space in the syringe; V_2 , volume of leachate sample in the syringe.

All sample determination was at least triplicated. ANOVA tests were applied to compare different treatments for N₂O production.

3. Results

3.1. Physicochemical properties of landfill leachate

Table 2 shows the physicochemical properties of the leachate samples. The temperature in raw leachate was high (26–37 °C), probably heated by the anaerobic degradation of MSW. Raw leachate was alkaline (pH 8.12–8.77). DO in raw leachate, storage ponds and anoxic treatment tanks were extremely low, mostly undetectable by the DO meter (detection limit 0.1 mg L⁻¹). However, DO levels were elevated to 0.6–8.0 mg L⁻¹ in the aerobic biological treatment processes. Significant COD and BOD₅ removals (88–98% and 75–94%, respectively) were achieved after leachate treatment.

3.2. Nitrogen dynamic in leachate treatment processes

Fig. 1 shows the changes in nitrogen concentrations during landfill leachate treatment processes. The NH₄⁺-N level in Datianshan raw leachate was the highest (5852 mg L⁻¹). Except Guoqiaowo Landfill, at least 80% of TN was NH₄⁺-N. A great portion of N in leachate was removed through the treatment processes (>84%), regardless of treatment methodology (Table 3). The highest percentage removal of NH₄⁺-N was in Xiaping landfill (>99.9%), where NH₄⁺-N concentration in the effluent was 0.11 mg L⁻¹.

Percentage composition of NH₄⁺ in TN in the Datianshan effluent was the highest (88.4%); in the other four landfills the values were 30.9%, 24.3%, 3.5% and 20%, respectively. The proportion of NO₃⁻-N in TN in raw leachate was 1.6%, 13.0%, 0.8%, 10% and 1.9% in Datianshan, Likeng, Shuikukeng, Guoqiaowo and Xiaping, but these figures increased to 13.3%, 98%, 5.6%, 34.3% and 50.6%, respectively, after aeration. The maximum NO₃⁻-N concentration (237.7 mg L⁻¹) was found in secondary aeration tank of Guoqiaowo Landfill. Relatively high NO₃⁻-N levels were observed in some other aerobic treatment processes, such as ozone treatment tank in Guoqiaowo (198.1 mg L⁻¹), aeration tank and oxidation ditch in Shuikukeng (161.8, 171.4 mg L⁻¹), biological aeration tank 1 and tank 2 in Likeng (134.5, 137.2 mg L⁻¹).

3.3. Nitrous oxide production from leachate treatment

Significantly high levels of dissolved N₂O and N₂O emission were detected in different leachate treatment processes (Table 4). Higher dissolved N₂O were generally found in the aerobic tanks and in the effluent. Among the five sites, the dissolved N₂O level in primary sedimentation tank of Likeng Landfill was the highest (1309 ng mL⁻¹). The dissolved N₂O concentrations in primary aeration tank of Likeng, aeration tank and effluent of Shuikukeng, aeration tank of Guoqiaowo, sequential batch reactor and effluent of Xiaping landfill were also very high. However, N₂O concentrations in leachate storage ponds and anaerobic

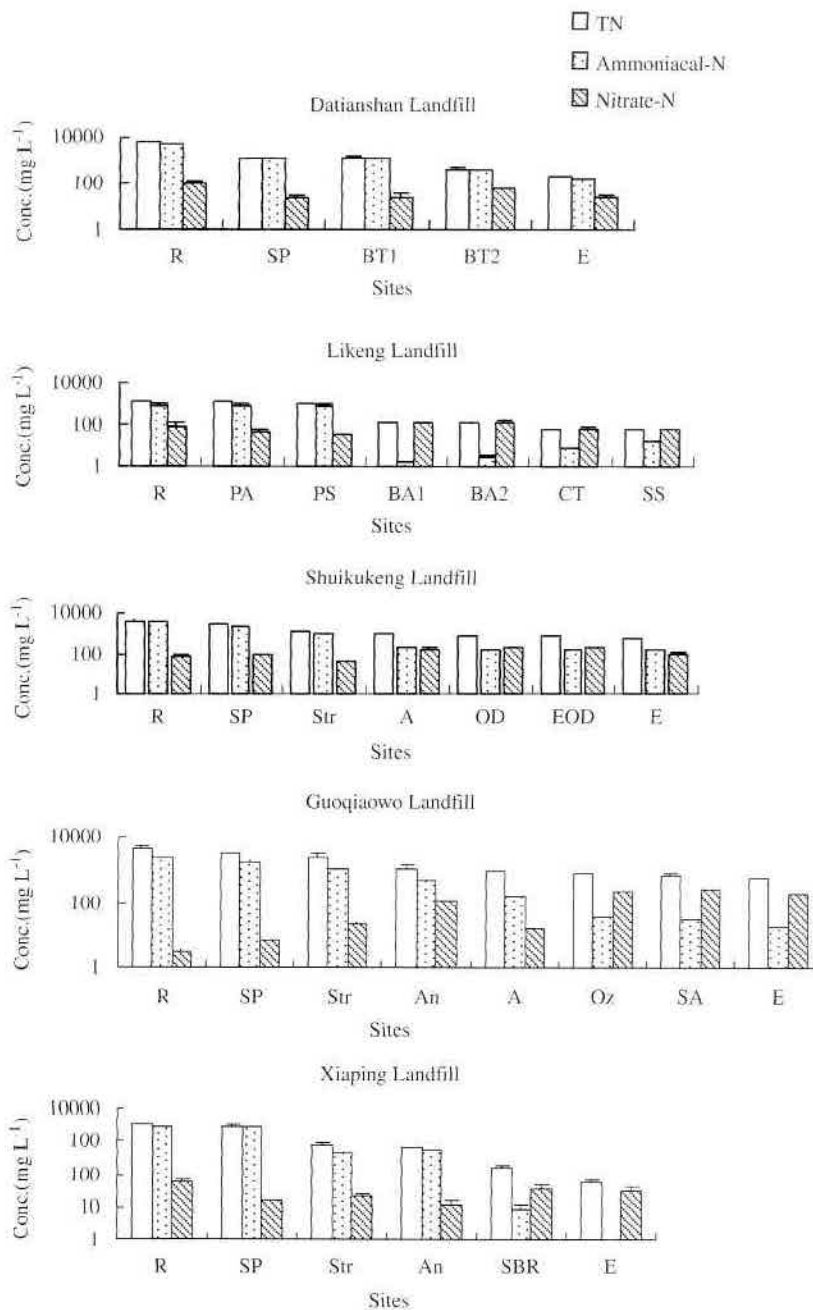


Fig. 1. Nitrogen concentrations in landfill leachate treatment processes.

treatment tanks were generally low. The quantity of N_2O emission from leachate showed a positive correlation with the dissolved N_2O content in leachate (Table 5). The highest N_2O emission ($58.83 \text{ ng mL}^{-1} \text{ water h}^{-1}$) was observed in the sequential batch reactor of Xiaping landfill (Table 4).

4. Discussion

4.1. Leachate treatment processes and N_2O production in leachate

Raw leachate samples collected from all the five sites had high level of NH_4^+-N ($630\text{--}5544 \text{ mg L}^{-1}$). High dissolved

N_2O and N_2O emission were found after raw leachate was aerated. Nitrous oxide production is a product of biological nitrification and denitrification; therefore, is highly correlated with the substrate (NH_4^+-N) level in the microcosm (Itokawa et al., 2001; Park et al., 2000). High partial pressure of O_2 favors nitrifiers to convert ammoniacal-N to nitrate-N ($NH_4^+ \rightarrow NH_2OH \rightarrow NO_2^- \rightarrow NO_3^-$), and low O_2 partial pressure favors denitrifiers to convert nitrate-N to nitrogen gas and release N_2O as a by-product ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$) (Gejlsbjerg et al., 1998; Itokawa et al., 2001). Liikanen and Martikainen (2003) suggested that O_2 was the key factor regulating the production of NO_3^- and enabling denitrifiers to produce

N₂O. It is generally accepted that a coupling between NH₄⁺ oxidation and NO₃⁻ reduction (nitrifier-denitrification) is responsible for the majority of the N₂O production during the leachate treatment. Positive correlations were, therefore, also detected between nitrate levels and DO levels in

the present study soon after the leachate was aerated and in the presence of nitrifiers and denitrifiers. Similarly, Kimochi et al. (1998), Park et al. (2000) and Yamagishi et al. (2001) reported that aeration causes N₂O production in domestic or synthetic sewage treatment. Anaerobic

Table 3
Nitrogen removal (%) by leachate treatment*

	TN removal (%)	NH ₄ ⁺ removal (%)
Datianshan	96.8	97.0
Likeng	90.8	97.3
Shuikukeng	84.3	95.5
Guoqiaowo	88.8	99.2
Xiaping	98.0	>99.9

*Removal (%) = (X–Y)/X, where X is the N concentration in raw leachate, Y is the N concentration in treated leachate.

Table 5
Pearson correlation coefficients between N₂O emissions from leachate and dissolved N₂O in leachate (P>0.05)

Landfill	Correlation coefficient
Datianshan	0.9993
Likeng	0.7769
Shuikukeng	0.9139
Guoqiaowo	0.9850
Xiaping	0.8689

Table 4
Dissolved N₂O concentrations in leachate samples and 24-h N₂O emission

Landfill	Treatment/sampling point	Dissolved N ₂ O (ng mL ⁻¹)		24-h N ₂ O emission (ng mL ⁻¹ h ⁻¹)	
		Average	SD	Average	SD
Datianshan	Raw leachate	2.07 a	0.10	0.048	0.003
	Storage pond	0.642 b	0.203	0.008	0.005
	Biological treatment 1	1.07 b	0.20	0.027	0.005
	Biological treatment 2	0.775 b	0.065	0.013	0.001
	Effluent	12.72 c	0.968	0.368	0.018
Likeng	Raw leachate	7.42 a	0.09	ND	0.004
	Primary aeration tank	180 b	31	45.8	25.1
	Primary sedimentation tank	1309 b	29	50.8	8.6
	Biological aeration tank 1	0.551 b	0.222	0.013	0.003
	Biological aeration tank 2	1.85 b	0.32	0.164	0.001
	Chemical treatment	45.8 b	4.7	1.35	0.00
	Secondary sedimentation tank	37.7 e	0.8	0.788	0.020
Shuikukeng	Raw leachate	13.9 a	1.02	0.202	0.225
	Storage pond	0.062 b	0.056	0.562	0.912
	Ammonia stripping	0.540 c	0.140	0.022	0.010
	Aeration tank	274 d	67	15.1	2.8
	Oxidation ditch	35.7 e	6.4	4.79	0.68
	Oxidation ditch effluent	131 f	17	5.93	0.37
	Effluent	499 f	138	14.6	5.5
Guoqiaowo	Raw leachate	2.08 a	0.23	ND	0.004
	Storage pond	18.6 b	3.1	0.005	0.016
	Ammonia stripping	7.12 c	2.06	0.104	0.059
	Anaerobic tank	4.20 c	0.77	0.092	0.019
	Aeration tank	125 d	2	26.7	4.0
	Ozone treatment tank	28.2 e	1.3	2.36	0.52
	Secondary aeration tank	24.4 e	7.1	1.83	0.62
	Effluent	21.2 b	2.0	0.712	0.038
Xiaping	Raw leachate	10.5 a	3.0	0.004	0.009
	Storage pond	2.08 b	0.72	ND	0.001
	Ammonia stripping	0.001 c	0.186	ND	0.002
	Anaerobic tank	ND c	0.082	0.250	0.387
	Sequencing batch reactor	219 d	68	58.8	1.1
	Effluent	154 d	10	9.19	1.81

Mean values in columns of each site denoted by different letters are significantly different (P>0.05).

ND: not detected.

leachate, similar to eutrophic lake sediment with low partial pressure of O_2 , therefore, is not active in N_2O production (Liikanen and Martikainen, 2003).

Nitrous oxide production could also be due to the NO_2^- reduction by NH_4^+ oxidizers under anoxic conditions (nitrifier-denitrification) with NO_2^- as electron acceptor (Poth and Focht, 1985). Hong et al. (1993) demonstrated that a decrease in C/N ratios resulted in increasing N_2O/N_2 ratios in the denitrification process. Therefore, N_2O could accumulate to a high level as an intermediate in leachate treatment due to inadequate concentrations of organic matter for complete denitrification. Schmidt et al. (2003) described more complicated microbial processes for nitrogen removal in wastewater. These processes include partial nitrification, nitrifier-denitrification and anaerobic ammonia oxidation (anammox). These studies revealed the multi-pathways of nitrogen conversion and N_2O production in nitrogenous wastewater, including landfill leachate. However, Gejlsbjerg et al. (1998), in a study of activated sludge, concluded that most of the N_2O produced was reduced to N_2 under anoxic conditions and most of the N_2O emission occurred under oxic conditions; coincided to the results of the present study.

Dissolved N_2O level did not increase after ammonia stripping and there was no signs that the ammonia stripping process would produce significant quantity of N_2O . However, ammonia gas is an air pollutant and direct emission to the ambient should be avoided (Berge et al., 2006).

4.2. Landfill leachate treatment as a point source of N_2O emission

High dissolved N_2O concentration in the leachate (up to $1390 \mu\text{g mL}^{-1}$) and N_2O emission from leachate (up to $50.8 \mu\text{g mL}^{-1} \text{ h}^{-1}$) were observed after anoxic raw leachate

was aerated. High concentrations of dissolved N_2O were also detected ($12.7\text{--}99 \text{ ng mL}^{-1}$) in effluent after leachate treatment. The levels were much higher than that detected in nature water (11.31 ng mL^{-1} , Great Canal, China; 0.36 ng mL^{-1} , Taihu Lake, China, in Xiong et al., 2002), from lab-scale intermittent aeration reactor (60 ng mL^{-1} dissolved N_2O ; $60 \mu\text{g L}^{-1} \text{ h}^{-1}$ for N_2O emission) and sewage treatment plants in Sweden ($9.1 \mu\text{g N L}^{-1} \text{ h}^{-1}$) (Table 6).

Per capita N_2O emission through landfill leachate treatment was estimated. The annual per capita average of MSW production in China was 440 kg (SEPA of China, 2000). The five landfills are equivalent to accepting the MSW of about 1.92, 1.51, 0.79, 0.22 and 1.92 million people for Datianshan, Likeng, Shuikukeng, Guoqiaowo and Xiaping, respectively. Although the percentage of N_2O transformed from the TN was low ($<0.0531\%$), annual N_2O emission from the five sites were estimated about 2.03–478 kg N_2O (Table 7). Therefore, N_2O emissions are expected to be 1.06, 6.6, 182.8, 63.4 and 249.2 mg $N_2O \text{ capita}^{-1} \text{ yr}^{-1}$ for the five sites, respectively. Kimochi et al. (1998) reported N_2O emission and nitrogen removal rates in domestic wastewater treatment in Japan. With intermittent aeration, most of the N_2O was emitted into the atmosphere during the aerobic period and N_2O emission was $0.43\text{--}1.89 \text{ g N}_2\text{O capita}^{-1} \text{ yr}^{-1}$; close to the results of present study.

The uncertainty in N_2O emission estimation is generally high. De Vries et al. (2003) noted that this is mainly due to the unsteady release through nitrification and denitrification to N_2O emissions. Nitrous oxide emission also highly depends on environmental temperature, atmospheric pressure, aeration and surface area of aquifer of concern. Biological N_2O production from leachate treatment work also depends on the characteristics of leachate, the design and the operation of the landfill site and also the composition of solid wastes (Chan et al., 1997; SEPA of China, 2004).

Table 6
Comparison of N_2O levels in different waters

Sampling sites	Dissolved N_2O	N_2O release	References
Sediment–water interface (laboratory microcosm)		$7.6 \mu\text{mol m}^{-2} \text{ d}^{-1}$	Liikanen and Martikainen (2003)
Lake Kevätön, Finland			
The Great Canal in Suzhou, China	$6110 \pm 270 \mu\text{g N L}^{-1}$		Xing et al. (2001)
Wells water, Suzhou, Chinab	$13,400 \pm 640 \mu\text{g N L}^{-1}$		Xing et al. (2001)
Taihu Lake, China	$0.36 \mu\text{g L}^{-1}$	$3.53 \mu\text{g dm}^{-2} \text{ h}^{-1}$	Xiong et al. (2002)
The Great Canal, China	$11.31 \mu\text{g L}^{-1}$	$0.122 \mu\text{g dm}^{-2} \text{ h}^{-1}$	Xiong et al. (2002)
Dairy farms wastewater treatment, Taiwan		$1.254 \text{ mg head}^{-1} \text{ h}^{-1}$	Su et al. (2003)
Rya sewage treatment plant, Göteborg, Sweden		Ave. = $9.1 \mu\text{g N L}^{-1} \text{ h}^{-1}$	Thörn and Sörensson (1996)
Nitrifying biofilm for wastewater treatment		Up to $0.083 \text{ g N-N}_2\text{O L}^{-1} \text{ h}^{-1}$	Garrido et al. (1997)
Soil-trench wastewater treatment process		$0.0082\text{--}0.0122$ (Japan) and $0.0033\text{--}0.0050 \text{ g N}_2\text{O L}^{-1}$ (China)	Kong et al. (2002)
Lab-scale intermittent aeration reactors	$60 \mu\text{g L}^{-1}$	$60 \mu\text{g L}^{-1} \text{ h}^{-1}$	Park et al. (2000)
Landfill leachate treatment processes in Guangdong, China	Up to $1309 \mu\text{g L}^{-1}$	Up to $58.83 \mu\text{g L}^{-1} \text{ h}^{-1}$	Present work

Table 7
Estimation of annual N₂O emission and percentage of total nitrogen transformed to N₂O emission from leachate treatment

	Datianshan	Likeng	Shuikukeng	Guoqiaowo	Xiaping
N ₂ O emission from leachate treatment (kg N ₂ O yr ⁻¹) ^a	2.03	9.89	144.4	13.94	478.5
Percentage of N in leachate transformed to N ₂ O ^b	0.0002%	0.0054%	0.0252%	0.0160%	0.0531%

^aSum of the potential N₂O emission from all the leachate treatment processes of a site, estimated from the 24 h static test, = $\Sigma \text{N}_2\text{O emission (ng mL}^{-1} \text{ water h}^{-1}) \times 24 \text{ (h)} \times 365 \text{ (d)} \times \text{annual leachate treatment capacity (ton)} / 10^6$.

^b = $\text{N}_2\text{O emission (ng mL}^{-1} \text{ water h}^{-1}) \times 24 / (\text{TN mg L}^{-1}) \times 1000$.

5. Conclusions

Nitrogenous landfill leachate treatment process can be a significant point source of N₂O production when anoxic raw leachate was aerated. Per capita N₂O emission from leachate treatment work is comparable with N₂O emission from conventional sewage treatment process. Ammonia stripping is a good option to remove a great proportion of NH₄⁺-N in landfill leachate before biological treatment where N₂O can be produced. However, the ammonia gas produced should be recovered and the direct flux of ammonia to the ambient should be avoided. Better leachate treatment technique is needed for complete mineralization of NH₄⁺-N in leachate to N₂ so that NH₄⁺-N will not be converted to any forms of green house gas or air pollutant.

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Life-cycle cost–benefit analysis of extensive vegetated roof systems

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Abstract

The built environment has been a significant cause of environmental degradation in the previously undeveloped landscape. As public and private interest in restoring the environmental integrity of urban areas continues to increase, new construction practices are being developed that explicitly value beneficial environmental characteristics. The use of vegetation on a rooftop—commonly called a green roof—as an alternative to traditional roofing materials is an increasingly utilized example of such practices. The vegetation and growing media perform a number of functions that improve environmental performance, including: absorption of rainfall, reduction of roof temperatures, improvement in ambient air quality, and provision of urban habitat. A better accounting of the green roof's total costs and benefits to society and to the private sector will aid in the design of policy instruments and educational materials that affect individual decisions about green roof construction. This study uses data collected from an experimental green roof plot to develop a benefit cost analysis (BCA) for the life cycle of extensive (thin layer) green roof systems in an urban watershed. The results from this analysis are compared with a traditional roofing scenario. The net present value (NPV) of this type of green roof currently ranges from 10% to 14% more expensive than its conventional counterpart. A reduction of 20% in green roof construction cost would make the social NPV of the practice less than traditional roof NPV. Considering the positive social benefits and relatively novel nature of the practice, incentives encouraging the use of this practice in highly urbanized watersheds are strongly recommended.

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Keywords: Green roof; Green building; Cost benefit analysis; Best management practices

1. Introduction

The relationship between the built and natural environment has traditionally been one of complete opposition. Both terrestrial and aquatic ecosystems are drastically, and often times irrevocably, altered during the process of urbanization (Pickett et al., 2001; Paul and Meyer, 2001). Water regulation and supply, erosion control and sediment retention, nutrient cycling, climate regulation, and waste treatment changes are all ecosystem services either eliminated or significantly degraded in highly developed landscapes (Costanza et al., 1997). The construction of man-made structures and impervious surfaces that are a defining feature of highly developed areas are an important

causal element behind environmental decline in urban areas (Arnold and Gibbons, 1996).

One reason why construction practices lead to environmental problems is that the costs of environmental degradation are not fully realized by the party who caused the damage. Thus, when evaluating construction costs, developers have historically viewed environmental damage as exogenous to the development process. Federal and state environmental laws have altered this situation to some extent in the last several decades. Developers have been limited by laws and regulations concerning erosion and sedimentation control, post-construction stormwater control and urban tree preservation. Nonetheless, developers still make land use decisions without considering the full cost of the environmental damage that their activities create.

Positive incentives have been developed for more ecologically sensitive development, particularly for buildings. A rating system called leadership in energy and

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environmental design (LEED) has been created by the United States Green Building Council for certification of commercial buildings that have a reduced environmental impact. As of 2005, 393 projects had received LEED certification and many municipalities require buildings built with public funds to receive LEED certification (Cassidy, 2003). Other organizations such as the National Association of Home Builders have recently developed green building guidelines based on similar standards (NAHB, 2004).

Specific building construction practices are being refined to create structures which have a much smaller impact on the surrounding landscape than previously thought possible. At the broadest scale, sites are selected for their proximity to public transportation, their ability to maximize open space and protect habitat, effectively manage stormwater runoff, address the heat island effect found in urban areas, and reduce light pollution (www.usgbc.org). Sustainable water use for a building may involve xeriscaping, graywater reuse for irrigation, and the use of low-flow or composting toilets and non-water urinals, which are becoming increasingly cost effective (Gleick, 2003). A building's energy use is also an extremely important component of sustainable design. From simply designing smaller structures to installing active solar panels or other on-site sources of self-supplied energy, there are a wide range of practices available to reduce a building's reliance upon fossil fuel energy sources. Increasingly, building materials contain recycled material content in new construction and attempt to reuse as much of the existing structure in renovations as possible (Horvath, 2004). Indoor environmental quality is also an important feature of green buildings. Paints and adhesives designated "Low-VOC" or "No VOC" (volatile organic compounds) reduces the low level toxic emissions found in older materials and improves indoor air quality for building occupants. Day-lighting larger portions of the structure improve the working environment in commercial buildings as well as reducing energy costs when high performance windows are used.

1.1. Designing rooftops for sustainability

Of these many ways that buildings can be designed and constructed in a more sustainable manner, the roof surface can easily be overlooked as space that can be designed into an environmental amenity for the building, not simply contributing to environmental problems. The rooftop is typically the same size as the building's footprint and is the structure's prime barrier against precipitation and solar radiation. To the extent that the roof surface can be transformed into useful space, the building becomes economically and functionally more efficient and can have a more benign effect on the surrounding landscape.

Published research has focused largely on the energy savings associated with different types of roofing systems. Akbari et al. (2001) found that changing a roof from one

with low albedo to high albedo in Sacramento, CA would decrease cooling energy use by 80%. Other studies have documented the affect of insulation on the heat flux at the roof surface (Al-Sanea, 2002), how to incorporate active and passive solar designs into rooftop systems (Heras et al., 2005; Maneewan et al., 2005), and the energy benefits associated with ventilated roof systems (Ciampi et al., 2005). These alternatives to traditional roofing systems are beginning to gain more of a market share and EPA has established an Energy Star rating system for roofing products, primarily identifying roofing membranes which have high albedos and the potential to significantly reduce building energy costs (www.energystar.gov).

While energy savings are an important function of alternative roof systems, other benefits may also be realized. In a traditional roofing system, rainfall hits the rooftop and is quickly channeled into the nearest gutter or storm sewer system with the goal being to have the roof shed water as quickly as possible. As regulations have mandated stormwater management plans for municipalities, rooftop runoff control has become an important management practice for minimizing degradation of aquatic ecosystems. One solution is to create rainwater storage tanks which can capture rainfall from the roof surface and store it for a time before it is reused or slowly discharged (Vaes and Berlamont, 2001).

1.2. Green roofs: multifunctional roof surfaces

The application of vegetation and growing media to the roof surface is an increasingly popular practice which produces improvements in both energy conservation and stormwater management. These green roofs are multifunctional in that they provide numerous environmental benefits simultaneously. These benefits include: decreasing the surface temperature of the roof membrane and energy use in the building (Kumar and Kaushik, 2005), retaining stormwater for small storm events (Carter and Rasmussen, 2006), increasing biodiversity and habitat in urban areas largely devoid of such space (Kim, 2004; Brenneisen, 2005), and improving ambient air quality (Clark et al., 2005). While these benefits are inherent in all green roof systems to some degree, depending on the design of the roof there is potential for other amenities as well. Accessibility and esthetic appeal for the building occupants, sound insulation and the potential for urban agriculture are all realistic benefits provided by green roof applications (Peck et al., 1999).

There are two general types of modern green roof systems: intensive and extensive. Intensive systems are characterized by deep (>6 in) growing media, opportunities for a diverse plant palate on the rooftop and high cost and maintenance requirements. Extensive systems are designed to be lightweight and easily retrofitted on existing roof surfaces. They contain thin growing media depths (2–6 in) and can support a limited number of drought-tolerant plants that thrive in the limited water and nutrient

conditions. Over 80% of green roofs in Germany are extensive systems and these types of green roofs are expected to offer the most cost-effective approach for roof greening (Harzmann, 2002).

1.3. *Economic analysis of green roofs*

While green roof projects have recently generated significant interest in design fields such as landscape architecture, little research has been done to evaluate the costs and benefits of green roof systems for urban applications. Much of the peer-reviewed literature on the economics of green roofing systems is found in conference proceedings and evaluate the private benefits at a single roof scale. Lee (2004) compared green roof and traditional roof life-cycle costs over 60 years for a single roof in Oregon. They found the green roof to be 7% more expensive than the conventional roof over this time. This analysis included extended roof life, energy savings, and stormwater fee reduction in the economic benefits that the green roof provided. Clark et al. (2006) demonstrated a return on investment of 11 years on a single green roof in Michigan when low green roof installation costs and high environmental benefits were considered. Alternative metrics to monetary values such as Eco-indicator values and energy analysis have been used to compare green roofs to conventional roofs in a sustainability context. These studies find green roofs provide significant environmental benefit over a traditional roof relative to the life cycle and embodied energy of its materials (Alcazar and Bass, 2006; Coffman and Martin, 2004; Kosareo and Ries, 2006). Other published reports typically focus on a single green roof benefit (Wong et al., 2003) or qualitatively describe a series of benefits derived from different types of green roofs (Peck et al., 1999; Banting et al., 2005).

Benefit cost analysis has been widely recognized as a useful framework for assessing the positive and negative aspects of prospective actions and policies, and for making the economic implications alternatives an explicit part of the decision-making process (Arrow et al., 1996). Benefit–cost analysis compares alternatives over time as well as space, and uses discounting to summarize its findings into a measure of net present value (NPV) (Hanley and Spash, 1993). The test of NPV is a standard method for assessing present value of competing projects over time. In the case of this study, the roofing scenario with the lowest NPV is the preferred option as the low value indicates the least costly alternative.

This study quantifies the costs and benefits of thin-layer, or extensive, green roof systems as they compare to typical flat roofs in an urban watershed. The authors combine local construction costs for an established green roof test site with experimentally collected stormwater retention data and building energy analysis data into a single metric using conventional cost–benefit analytical techniques applied over the life cycle of a typical green roof. In order to carry out this analysis we rely in part on published data

from other green roof research and practice for estimating these effects. This may introduce some bias, and indicates that this work is subject to revision as increasing experience with green roofs produces more and better data. We then use this information to evaluate an entire local watershed, using a variety of spatial scales as a case study for application of widespread green roofs. As green roof popularity continues to grow, it is important for accurate life-cycle benefit–cost analyses (BCA) of green roof systems to be performed to inform both policy makers who may allocate public funds for projects with public benefits, and private building owners who may see a future financial incentive to invest in new and relatively unproven technology.

2. Materials and methods

2.1. *Project site and test plot*

The project examines the feasibility of replacing all the flat roofs in an urban watershed with green roof systems. The Tanyard Branch watershed was selected as a study site. This highly urbanized watershed contains a second-order stream system and is located in Athens, GA approximately 60 miles east of Atlanta, GA. The watershed contains significant portions of the downtown commercial district of Athens, the University of Georgia, and both single and multi-family residential areas. Using 2003 aerial photography, the impervious surfaces including rooftops were digitized into a geographic information system (GIS). About 53.8% of the land cover is impervious surface with rooftops accounting for 15.9% of the total land cover in the watershed (Fig. 1). The Tanyard Branch creek is listed as not meeting its designated use due to elevated fecal coliform counts with the cumulative effects of urbanization in the watershed cited as the cause of this degradation (Herbert, 2003). Flat roofs are the most viable candidates for greening as they often require no additional structural support and minimal design expertise for green roof installation (Banting et al., 2005). Flat roofs constitute 176,234 m² or 7.4% of impervious surface in the watershed (Fig. 2).

A 42.64 m² green roof test plot was established in October 2002 on the campus of the University of Georgia (Fig. 3). The test plot was designed to be simple to build and easy to replicate using American Hydrotech's extensive garden roof. American Hydrotech, Inc. is a single source supplier for the specialized green roofing materials. These materials included a WSF40 root protection sheet, an SSM 45 moisture retention mat, a Floradrain FD40 synthetic drainage panel, and a Systemfilter SF geotextile filter sheet (American Hydrotech, 2002). The growing media was a Lightweight Roof Garden mix provided by ItSaul Natural, LLC. This soil mix is a blend of 55% Stalite expanded slate, 30% USGA sand, and 15% organic matter composed primarily of worm castings. This mix was spread to a depth of 7.62 cm. Six drought-tolerant plant species were selected for their ability to survive low nutrient

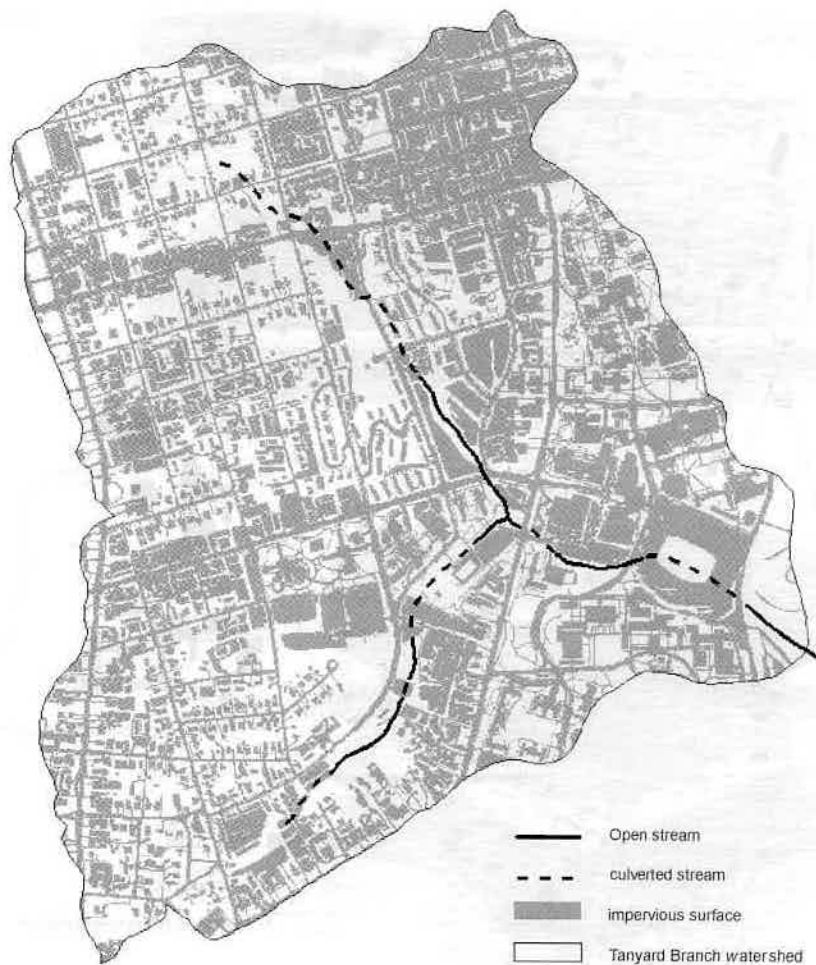


Fig. 1. Tanyard Branch watershed impervious cover and stream network.

conditions and extreme temperature fluctuations found at the roof surface. No irrigation or fertilization was applied except for the initial three days of planting.

2.2. BCA framework

Green roof BCA was performed according to an 8-stage framework found in Hanley and Spash (1993). The stages are: definition of project, identification of project impacts, identification of which impacts are economically relevant, physical quantification of relevant impacts, discounting of cost and benefit flows, application the NPV test, and sensitivity analysis.

2.3. Discounting of benefit and cost flows and sensitivity analysis

The period of analysis was one green roofing cycle, which was estimated to be 40 years based on the doubling of the roof life due to the vegetated cover. Private BCA for greening a single flat roof of 929 m² as well as a social BCA of greening all the flat roofs in the watershed was performed. All roof greening occurred at year zero. Traditional roofs were greened at year zero and also

underwent one reroofing cycle at year 20. Avoided storm-water costs were applied at year zero. Energy and air-quality benefits were applied every year of the analysis. A discount rate of 4% was applied to the reroofing scenario as well as all the green roof benefits.

3. Theory and calculation

The economically relevant impacts of widespread roof greening were established and physical quantification of these impacts were performed using the green roof test plot as a template for all new green roofs in the watershed. The benefits were divided into categories found in Table 1 with the conceptual framework outlined in Fig. 4. Analysis for the social BCA was performed at the watershed scale while a private BCA was performed using a typical one-story 929 m² roof. Details of each category follow below and the results are summarized in Table 2. All dollar amounts have been converted to \$2005 using the consumer price index.

3.1. Construction and maintenance

The first category deals with construction and maintenance expenses. The construction costs of a typical

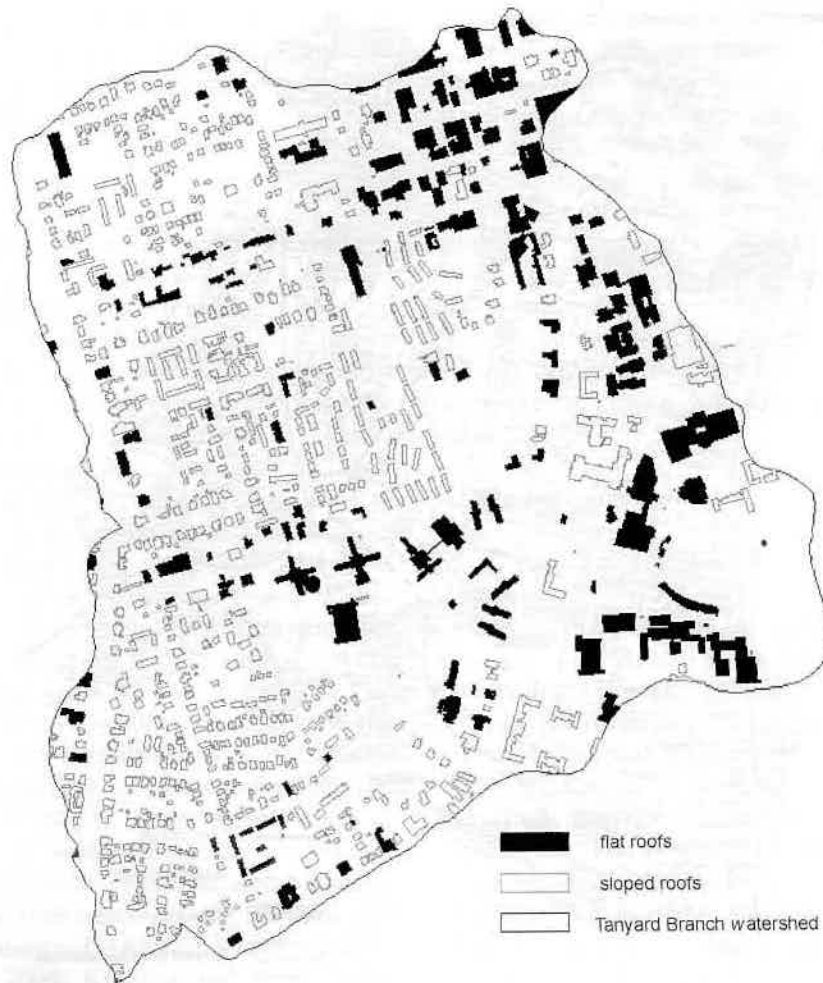


Fig. 2. Rooftops in the Tanyard Branch watershed.

built-up bituminous roof system on a concrete roof deck were taken from personal interviews with three local roofing contractors and additional verification from the Means Construction Cost Data (2005). The traditional roof was assumed to have a 20-year guarantee on the waterproofing membrane and thus an effective 20-year life before replacement. The construction costs of a conventional roof were estimated to be \$83.78/m².

The cost estimate on the green roof was obtained from the test site as well as personal interviews with three single source green roofing manufacturers. The average cost from these sources was compiled into a unit cost estimate of for initial construction of an extensive (7.62 cm of growing media) roof system. No additional waterproofing cost was added. While each installation would not have identical costs depending on accessibility, structural integrity, and design considerations, an estimate of \$158.82/m² was used based on average costs from the manufacturers and the local test plot (Table 3). Maintenance on a thin-layer green roof is considered equivalent to the maintenance schedule of a traditional roof with visual inspections twice per year. Many industry groups

claim green roofs can extend the life of the waterproofing membrane over 200%. This is due to the vegetation and growing media protecting the membrane from harmful ultra-violet radiation and physical damage. Since green roofs have only been used extensively in the United States in the past decade and there are few examples to verify this claim. However, engineered green roofs in Europe have been shown to function for over twice the life span of conventional roofing systems (Köhler et al., 2001). For this study, green roofs are assumed to last for 40 years—twice the life span of conventional roofs.

While the unit construction cost of \$158.82/m² is used for our base case analysis, this most likely is at the high end of what would be experienced for widespread green roof construction in the Tanyard watershed. It is partially based on estimates of what would be required to build an initial demonstration roof, and thus ignores economies of scale in materials purchasing as well as innovations in construction techniques developed as local contractors gained experience. Second, in Germany where the industry has been established for over 30 years, construction costs may be as much as 50% lower for larger installations (www.greenroofs.com).

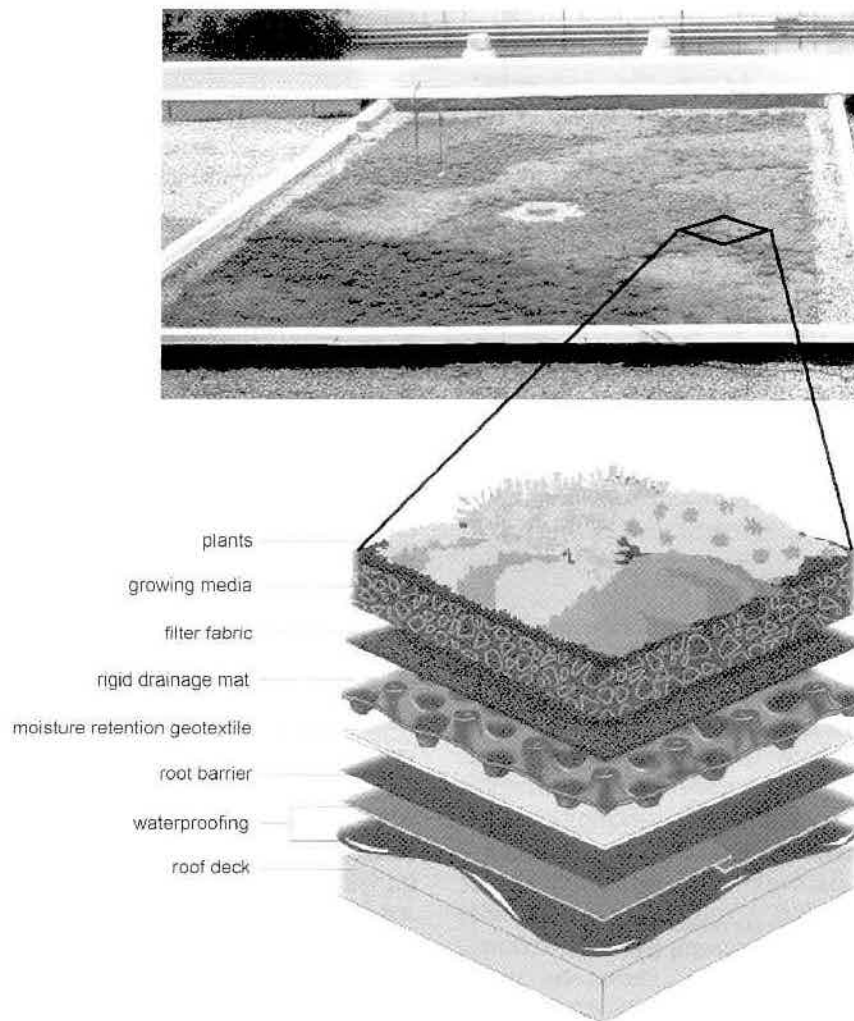


Fig. 3. Green roof test plot and layer cross-section.

Table 1
Benefits from extensive green roof systems

Category	Benefit	Quantified?
Construction and maintenance Stormwater management	Double the roof life	Yes
	Storm sewer pipe size reduction	Yes
	Reduces need for alternative stormwater BMPs	
Energy and insulation Air quality Habitat/greenspace	Stormwater utility fee reduction	
	Additional insulation	Yes
	Energy savings	Yes
Urban heat island	Nitrogen oxide uptake	Yes
	Increase bird and insect habitat	No
	Reduction in ambient air temperatures	No

It is therefore assumed that true construction costs will vary between 50% and 100% of this initial estimate when the sensitivity analysis is performed.

3.2. Stormwater management

Stormwater management is a second economically relevant category. Under the US Environmental Protection Agency's National Pollutant Discharge Elimination System (NPDES) Phases I and II stormwater rules, jurisdictions with municipal separate storm sewer systems (MS4s) are required to develop a stormwater management program relying upon stormwater best management practices (BMPs) to control stormwater discharges. Green roofs may potentially be one of the BMPs used to accomplish the goals of this program. Green roofs have been shown to retain a significantly higher percentage of stormwater when compared to a traditional roofing system. A recent study in Michigan documented how, during medium volume rain events, a thin-layer green roof system retained 48% more rainfall than a gravel ballast roof (VanWoert et al., 2005). The local test roof was monitored for its ability to retain stormwater from November 2003–November 2004. The green roof retained, on average, more than 77% of the rainfall throughout the year with retention performance determined primarily by total storm

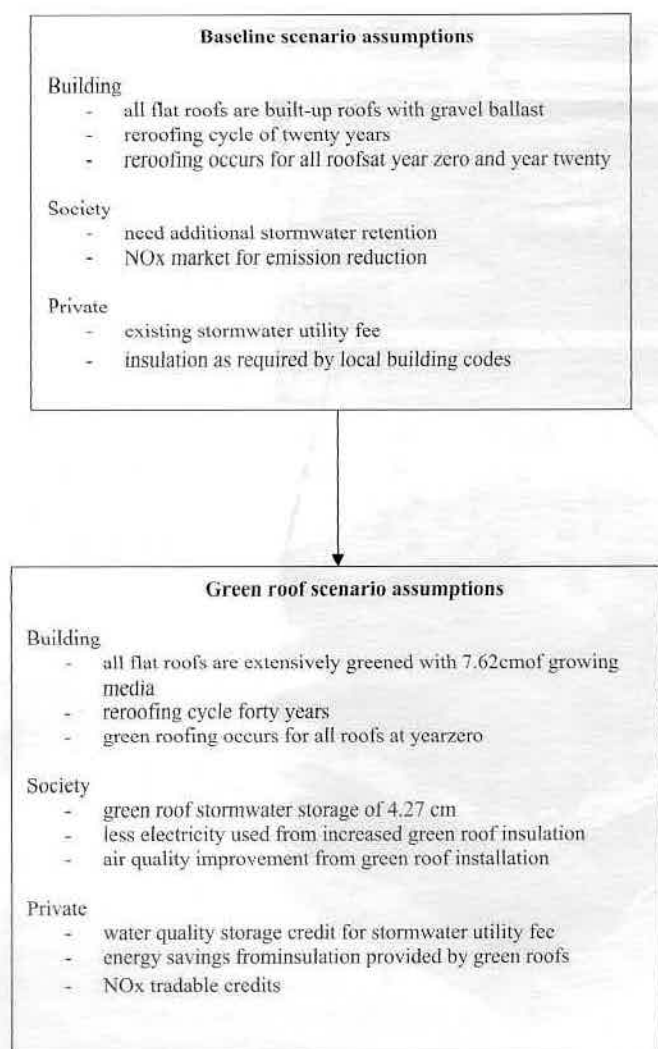


Fig. 4. Modeling assumptions for private and social BCA.

Table 2
Costs and benefits per square meter of roof

	Year	Unit values (\$/m ²)
Cost		
TR construction and maintenance	0.20	83.78
GR construction and maintenance	0	155.41
Social benefits		
Avoided stormwater BMP cost	0	9.06
Energy	1–40	0.37
Air quality	1–40	0.11
Private benefits		
Stormwater utility fee credit	1–40	0.04
Energy	1–40	0.37
Air quality	1–40	0.11

rainfall volume. Details from this study can be found in Carter and Rasmussen (2006).

Using the stormwater retention performance data and watershed spatial information, total additional stormwater

Table 3
Additional green roof unit construction costs

	Cost range (\$/m ²)	Cost used (\$/m ²)
Specialized roofing material	5.92–32.61	32.61
Growing media	5.62–6.78	6.59
Plants (21 plugs/m ²)	9.69–10.12	9.69
Crane rental	14.90	14.90
Labor	7.84	7.84
Total	43.97–72.25	71.63

Table 4
Avoided cost of urban BMPs (source: EPA, 1999)

BMP	Cost (\$/m ³ treatment)	Total cost (\$) using flat green roof storage in Tanyard Branch
Bioretention area	232.37	1,752,593.21
Porous pavement	141	1,063,461.04
Sand filter	263.09	1,984,319.06
Equal distribution of the three BMPs	212.15	1,600,124.44

storage from greening all flat roofs could be estimated for Tanyard Branch. The spatial analysis was done using ArcView 3.2, a commonly used GIS software package (ESRI, 1999). 2003 full color aerial photographs with 0.15 m pixel resolution were obtained from the city of Athens. From these photographs, flat roofs in the watershed were digitized at a scale of 1:500 (Fig. 2). Ground-truthing was also performed. Extensive greening provided an additional 4.27 cm of stormwater storage depth which results in total storage for the watershed of 7542 m³. This retention data then compared with published retention and cost data from other stormwater BMPs for determining the cost for an equal amount of storage using other practices given the land cover in the watershed (EPA, 1999). Since the watershed is already highly urbanized, only BMPs which are typically used in an ultra-urban application were considered. These BMPs include sand filters, bioretention areas, and porous pavement. Depending on the type of BMP used in the comparison, different cost savings may be realized (Table 4). The avoided cost of using alternative stormwater BMPs is considered part of compliance with Phase II stormwater rules in Athens and the benefits are included in the social BCA. Analysis was run by dividing the total stormwater storage volume provided by green roofs equally among the three alternative BMPs and calculating the total cost of this alternative scenario (Table 4).

An additional private stormwater benefit for green roofs may be realized in the regulatory arena. Increasingly, jurisdictions are creating stormwater utilities, which are charge fees to parcel owners based on their parcel's stormwater contribution to the system. These utilities generate income used exclusively for stormwater management operations. Parcel owners are commonly given

exemptions or credits if they can demonstrate that they are keeping their site from contributing runoff to the stormwater system. Athens has enacted a stormwater utility and incorporated a system of credits for demonstrated on-site management. With the proper documentation, green roofs are assumed to accomplish the water quantity standards required for the stormwater credit. In the case of the roofs in Tanyard Branch, this results in a savings ranging from \$0.04/m² to \$0.08/sm depending on building type (Table 5). Calculations were performed based on the spatial information of the buildings in the watershed. The majority of the savings came from commercial, government, and multi-family buildings with the average unit cost being \$0.04/m². The total value was applied to the private BCA. This is a transfer payment which does not increase social welfare and therefore is not included in the social BCA.

Another aspect of stormwater management is the drainage collection of pipes, inlets and junction boxes collectively termed the storm sewer system. Retention of stormwater before it reaches the system may result in resizing of the pipes during maintenance and repair of the infrastructure. Athens contains an MS4 and spatial data for the storm sewer system was acquired for the watershed from the city of Athens and the University of Georgia. Stormwater pipes in Athens-Clarke County are a minimum of 38.1 cm (15 in) and most are designed for the 25-year storm event, which in Athens is 15.85 cm. Pipe costs were estimated according to Means (2005) with unlisted pipe dimensions priced using the power function derived from Means (2005):

$$C = 0.6318D^{1.4086},$$

where C is the cost of pipe (\$/lf) and D the diameter of the pipe (in).

Reductions in the storm flow volumes from the watershed outfall were calculated for a variety of storm events using StormNet Builder, a comprehensive stormwater modeling package (Boss International, 2005). This study is detailed in Carter (2006). The cost savings from a reduction in pipe size was then calculated and converted to a cost per linear meter of pipe. This cost saving showed a 4.6% reduction in size for the 25-year event and a 4.4% reduction for the 100-year event. These reductions are not significant enough to result in changes in pipe sizing due to green roof implementation; therefore no economic benefit from pipe resizing was used in the analysis.

Table 5
Stormwater utility benefits by building type

Building type	Benefit (\$/m ² /year)	Total annual benefit in Tanyard Branch (\$)
Commercial	0.04	3306.65
Government	0.04	3908.66
Multi-family residential	0.04	1003.02
Single family residential	0.08	28.47
Total		7485.95

Other relevant features of stormwater management affected by widespread green roof implementation were determined not to be applicable to this particular watershed. Included in this is the effect of green roof stormwater retention on the reduction of combined sewer overflows (CSOs), a phenomenon having large environmental impacts resulting from the stormwater systems found in many larger cities. It was estimated in the city of Toronto, for example, that avoiding CSOs using green roofs would save the city \$46.6 million in infrastructure savings (Banting et al., 2005). Athens, however, has separate sewer systems for stormwater and waste water and therefore this analysis could not be performed. Also, a reduction in nuisance flooding, which is a commonly quantified through flood insurance premiums, is not appropriate for this stream system as the stream is piped or highly incised with no flood risks in the residential sections of the watershed.

3.3. Energy and insulation

The third economically relevant category is energy and insulation. Green roofs act to reduce the rooftop surface temperatures through leaf shading direct solar radiation, evaporation of moisture at the surface and transpiration of the plants which cool the ambient air above the roof. Thin-layer green roof systems have consistently been shown to reduce the temperature fluctuations at the roof surface (Onmura et al., 2001). Whether this translates into significant energy savings is not clear from the literature as in one study, energy use was evaluated for small experimental sheds containing green roofs and the vegetated treatments had little effect on total energy use in each structure (DeNardo et al., 2003). Other research, however, suggests that considerable energy cost savings can be realized when green roofs are used; enough for the life-cycle cost of a green roof to be less than a traditional roof when energy savings were included in the analysis (Wong et al., 2003).

For the energy-related benefits in this study, local data were used. Adjacent to the stormwater green roof test plot, a second experimental roof was constructed and an analysis of the thermal conductivity of growing media as well as energy load modeling was performed. Automated measurement of in situ micrometeorological parameters such as humidity, air temperature, windspeed, radiation, and soil temperature were combined with laboratory analysis of the engineered growing medium providing local data for simulation modeling. The simulation programs used were eQuest and HYDRUS-1D, a building energy model and a combined heat and moisture simulation, respectively. The modeled buildings used were 929 m² with both square and rectangular orientations. Modeling was performed at three different heights: 1, 3, and 8 stories. Additional details from this study can be found in Hilten (2005). Cost savings from the additional insulation provided by the green roof as well as the reductions in the

heating and cooling loads were found for the building and converted into unit savings to be applied across the watershed. The green roof's insulating value was equivalent to R-2.8, which is similar to 2.54 cm of fiberboard, fiberglass, or perlite. These types of insulation average to \$3.98/m² and this value may be considered an avoided cost in the green roofing analysis. If this avoided cost is used, however, the building owner will not realize any energy savings as there is no net increase in insulation.

A more likely scenario is that the green roof will be added and provide additional insulation, not used as replacement for traditional insulation. This additional insulation value creates energy savings for the building owner. The authors used the building energy savings modeled from a single-story 929 m² building (Hiltner, 2005). This type of building was selected because it represents the majority of flat-roofed buildings in the watershed. The energy load reduction from the green roof system was modeled at 4222.56 kWh/year. This is an energy savings of 3.3% which is less than half of the 8% used in the Wong et al. (2003) study. Residential rate surveys for the 2005 year were acquired from the Georgia Public Service Commission and the 2005 average rate of \$0.082/kWh was applied to the energy savings modeled in the building. This current price is used for the conservative base case BCA, but we believe that assuming electricity prices will remain constant in real terms over the next 40 years is extremely optimistic. Policies to limit air pollution and climate change are likely to bring about significant increases in this price. For the sensitivity analysis, it is assumed that the actual rate of increase in energy prices will vary on a uniform distribution between 0% (the base case assumption) and 8% (a pessimistic but plausible assumption under significant future environmental regulation). All buildings in the watershed were estimated to have the same energy savings, although savings may vary based on the number of stories and orientation of each structure. The unit energy savings for current energy rates was \$0.37/m² (Table 6).

3.4. Air quality

A fourth economically relevant category is air quality. While the potential may be great for green roofs to improve air quality in densely developed areas, the type of vegetation found on the rooftop largely determines the

amount of air-quality improvement. Trees, grasses, and shrubs both filter pollutants and transpire moisture much differently than the Sedum plant species commonly found on modern green roof applications. Cross-applying air-quality improvements from one type of green roof application to another can be very misleading. For example, air-quality benefits have been modeled for grass roofs in Toronto with the authors finding significant economic benefits to air quality under grass roofing scenarios (Currie and Bass, 2005). The Georgia test plot, however, was designed to be simple and easily replicable using Sedum plants. These plants do not have the same leaf area index, photosynthetic activity, or growth pattern as grasses thus making this particular air-quality benefit unsuitable for this study.

Other researchers evaluated nitrogen oxide uptake made by the *Crassulaceae* plant family of which Sedum is a member (Sayed, 2001). While this CO₂ uptake is well documented, the air-quality improvements provided by the function are less certain, but basic estimates for economic quantification of these improvements are possible by including Sedum green roofs as part of a cap-and-trade emissions credit system. Using 2005 market value for NO_x emission credits of \$3375/ton, Clark et al. (2005) estimated the credit for a Sedum green roof to be \$0.11/m². This value was applied to the current analysis as the air-quality benefit since it was deemed more appropriate for the roof system used in this study. Both the private and public sectors benefit from this technology as green roofs reduce the pollutant loads in the ambient air of the city improving social welfare while allowing the private building owner to receive economic compensation from providing a service for industries looking to offset their polluting activities.

3.5. Unquantifiable categories

Other categories may be economically relevant in particular green roof applications, but were not included in this analysis either because of a lack of reliable data or incompatibility of the benefit with the type of green roof used in this study. Urban green space and habitat is clearly a benefit provided by green roofs and rooftop greening has been incorporated into plans to maintain urban habitat networks (Kim, 2004). Valuation of urban greenspace is typically done through hedonic analysis relating house prices to greenspace type and location (Morancho, 2003). While accessible rooftops provide the building owner or tenant with additional space for recreation or growing vegetables, the roof designed in this study does not perform these functions. The greenspace value must be derived strictly by the habitat value for biotic communities on the roofs themselves which is difficult to quantify and outside the scope of this project.

Urban centers have air temperatures higher than surrounding rural areas, a phenomenon commonly known as the urban heat island. In theory, since green roofs reduce

Table 6
Energy benefits associated with green roofs

Benefit	
Building energy savings (kWh/year)	4222.56
Energy cost (\$/kWh)	0.08
Building energy savings (\$/m ² /year)	0.37
Total annual savings in Tanyard Branch (\$)	65,871.73

the surface temperature of the rooftop, the ambient air temperature is lowered thus reducing the heat flow into the building and concomitant energy use needed to maintain comfortable interior building temperatures. Energy models demonstrate that widespread roof greening could lower temperatures city-wide by 0.1–0.8° Celsius, a negligible amount considering the uncertainty in the models (Bass et al., 2003). Until more robust studies demonstrate otherwise, the energy cost savings from reducing the urban heat island due to widespread roof greening will be considered speculative and not included in this analysis.

4. Results

4.1. Green roof private and social benefits

Green roof benefits were estimated for both private and social institutions. Results from these runs are shown in Tables 7 and 8. The benefits are considered conservative estimates where current pricing conditions are assumed and values base on the campus test plot are used.

4.2. Applying the NPV test

Compiling all the discounted costs and benefits associated with these two roofing systems allows for an NPV

Table 7
Conservative green roof social benefits (\$) at the watershed scale

Green roof benefit	Unit benefit (\$/m ²)	4% discount rate
Avoided BMP cost	9.06	1,600,124.44
Energy	0.37	1,306,318.84
Air quality	0.11	377,046.09
Total social benefits	9.54	3,283,488.37

Table 8
Conservative green roof private benefits for a 929 m² roof

Green roof benefit	Unit benefit (\$/m ²)	4% discount Rate (\$)
Stormwater utility credit	0.04	780.80
Energy	0.37	6870.53
Air quality	0.11	1983.06
Total private benefits	0.52	9634.38

Table 9
Comparison of green and conventional roof NPV

	Private roof (\$)		Public watershed (\$)	
	Conservative	Average	Conservative	Average
Green roof costs	144,378.20	108,474.13	27,451,153.64	20,624,589.43
Green roof benefits	9634.38	19,040.24	3,283,488.37	5,077,495.58
Green roof NPV	134,743.80	89,433.89	24,167,665.27	15,547,093.85
Conventional roof NPV	113,352.95	113,352.95	21,552,206.10	21,552,206.10
Green/black roof cost ratio	1.19	0.79	1.12	0.72

test to be performed. Using a 4% discount rate over 40 years, the total costs of installing thin-layer green roof systems on the flat roofs in the Tanyard Branch watershed are \$27,451,153. The total costs of traditional built-up roofing systems the over this same time period is \$21,552,206. If an equal distribution of all three stormwater BMPs across the watershed is assumed, social benefits equal \$3,283,488.37 and a social NPV of \$24,167,665 which is 12.14% more than traditional roofing (Table 9).

The private analysis performed on an individual roof shows NPV of green roofs to be relatively more costly for the building owner when compared with the social BCA. Private costs differ in that they include a stormwater utility fee credit rather than avoided stormwater BMP costs. This results in a total construction cost of \$144,478 for green roofs and 113,353 for conventional roofs at a 4% discount rate on a 929 m² building. Total private benefits from green roofing for the private building totaled \$9634. This is 18.87% more than typical roofing.

4.3. Sensitivity analysis

The NPV test was recalculated with changes to various key parameters for sensitivity analysis. Sensitivity analysis helps determine on which parameters the NPV outcomes depend the most (Hanley and Spash, 1993). The parameters were allowed to vary randomly between ranges of expected values over 10,000 trials. An average value from these trials was then calculated and compared with values found for the green roof NPV base case (Fig. 5). Sensitivity analysis was run for both the private and public green roofing scenarios.

The first parameter was the discount rate. Discount rates were modeled around the initial 4%, between the rates of 2% and 6%. Another key parameter was roof construction costs. As the industry continues to mature in North America it is likely that initial construction costs will decrease. Analysis was run with the cost of the green roofing system ranging from the existing cost to a 50% reduction in green roof construction costs. Finally, volatility in energy prices was considered with energy prices ranging from existing prices to a yearly increase of 8%.

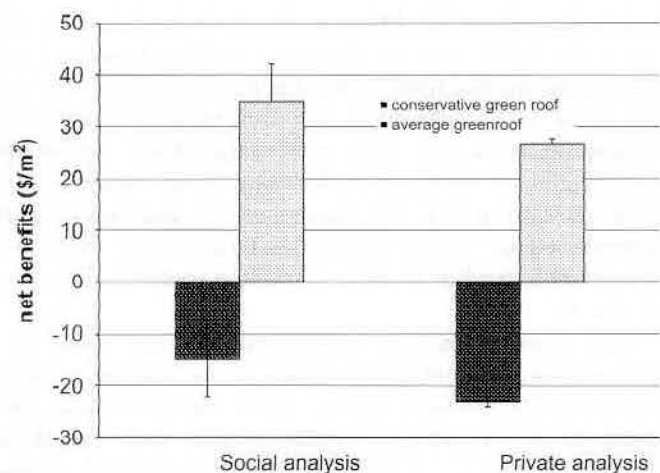


Fig. 5. Comparison of conservative and average net benefits for private and social green roofing scenarios.

Our sensitivity analysis is asymmetric, that is while discount rates vary around the central estimate, both green roof construction costs and energy costs vary only in the direction that is more sympathetic to the economics of using green roofs relative to conventional roofs. This is done because the current point estimates are in fact at the extremes. Green roofs are not going to be more expensive than our demonstration roof under conditions of dramatically increased construction, and electricity prices are not going to be lower than current prices given the expected course of environmental regulation and energy supply and demand. The assumptions used in this sensitivity analysis give a better picture of what the real economics of green roof construction are likely to be, while the base case estimate is a conservative or almost-worst-case scenario.

The results from the sensitivity analysis demonstrated that given realistic assumptions about the changes in the costs and benefits of implementing green roof systems, the average NPV of green roofs is less than the current NPV of black roofs meaning that over the roof's life cycle it is cheaper to install green roofs than their traditional counterpart. The most important parameter was the construction cost estimate, which averaged \$116.76/m², down from \$155.41/m². Change in green roof benefits due to increased energy prices translated into significantly more energy benefits over the life cycle of the roof, up to \$17.46/m² from \$7.32/m². In total, the average social benefit from using green roofs totaled \$34.95/m² and the average green roof private benefit was \$26.70/m² using the mean values created by the sensitivity analysis (Fig. 5). Comparing the cost ratio between green and traditional roofing for the conservative NPV estimate and the average estimate generated by the sensitivity analysis show green roofs drop \$0.40 on every dollar down to \$0.79 from \$1.19 for the private scenario and down to \$0.72 from \$1.12 when social accounting is performed (Table 9).

5. Discussion

BCA of widespread extensive roof greening in the Tanyard Branch watershed reveals a number of important considerations for both the private and public sectors when considering green roof installation. The most significant economic benefits are the increase in roof life, stormwater BMP cost avoidance, and energy savings. The main construction benefit, and best overall benefit in economic terms, of the extensive green roof is that it extends the life of the waterproofing membrane and eliminates the need for frequent reroofing. Without this benefit, green roofs would cost over 85% more than their traditional counterpart. One problem in realizing this benefit is that many waterproofing companies will still only guarantee their premium membranes for 25 years, which may reduce the incentive for a building owner to invest in a green roof during initial construction. As long-term green roof projects are built and monitored, more experience and ultimately green roof life warranties may help institutionalize this benefit.

Avoiding the cost of other more expensive stormwater BMPs is an important green roof benefit. Since green roofs do not consume valuable urban land, there is no opportunity cost associated with them as there may be with other stormwater BMPs such as bioretention areas. Additionally, green roofs are independent of watershed soil type. They can be implemented anywhere there is a building as opposed to porous pavements, for example, which must have adequate soil permeability before installation is possible (Ferguson, 2005). This analysis demonstrates that green roofs are most practically implemented in densely developed urban centers where other practices are impossible or cost-prohibitive. This stormwater benefit is also public, accomplishing water quality and quantity goals for the jurisdiction, and therefore justifies the use of public funds to encourage private building owners to use green roofs for stormwater mitigation.

Annual energy savings for building owners total over \$65,000 in the watershed. While not as significant as extended roof life, this private benefit will be continuously realized each year and help offset some of the initial upfront cost for the building owner. If the building is rented, as many commercial structures are, the tenant will receive this savings. This benefit may function as a marketing tool for the building owner to attract new tenants when leases are renewed. Given uncertainties about energy prices due to the possibility of increased regulation due to air quality and climate change concerns, it is possible that the conservative case has significantly underestimated these benefits. Sensitivity analysis shows that increasing energy prices would result in over \$3,000,000 savings over the life cycle of the roof.

The benefit to the existing storm sewer system in the Tanyard Branch watershed is relatively small in economic terms. This is primarily due to the nature of the stream system and the type of sewerage found in the watershed.

The highly impacted urban stream shows little potential for economically quantifiable improvement strictly with green roof implementation. Much of the stream is piped and culverted with no change in the sizing of these facilities when green roofs are implemented. This is because extensive green roofs are highly effective at retaining stormwater for small storm events with recurrence intervals of 1–2 years, but are less effective at retaining significant portions of runoff from the larger 25–100-year storms. Stormwater systems are typically designed for these larger storm flows.

Additionally, the flood mitigation benefit is minimal. The geomorphology of Tanyard Branch creek has been dramatically altered by urbanization to the point, where the incised banks will only flood on a recurrence interval of a few billion years or effectively never for the purposes of this study (Herbert et al., 2003). There may potentially be marginal improvement in the stream ecosystem with reduction of sediment transport capacity and reduced volume and frequency of runoff from small storm events. Contingent valuation studies or hedonic property valuation of these improvements are difficult as the majority of the day-lit stream reaches are on a single parcel of the campus of the University of Georgia. These site-specific conditions are important qualifiers that may not be true when evaluating green roof benefits in other watersheds. In addition, caution should be used in making inferences based on these results because construction and maintenance techniques, as well as estimates of their energy-saving, stormwater-retention, and air-quality improvement benefits, may change as greater experience brings both innovation and better information.

Sensitivity analysis demonstrates that application of green roofs under varying market conditions can significantly influence whether or not green roofs pass the NPV test when compared to traditional roofs. The base green roofing case used in this analysis is more of a “worst case scenario” than a realistic picture of future green roof installations. The average costs represented in the sensitivity analysis may be a more realistic picture of the pricing that future green roof installers will face. Since construction costs are the most likely of the parameters to decrease as well as the most influential in the NPV performed in this analysis, the conditions appear favorable for thin layer green roof systems to become more profitable than built-up asphalt roofs with further cost reductions among firms in the industry. Direct production and specialization in Germany has led to low unit costs of green roofing materials relative to the United States. A reason for this is that many of the single-source green roof suppliers in the United States simply are dealers of green roof products imported from German green roof companies, which increases the total cost of these materials. Further maturation of the industry in the United States should expand opportunities for more efficiency and price reductions across the spectrum of green roof products and services.

6. Conclusions

Expansion of urban areas and the built environment, combined with greater public interest in maintaining the integrity of ecological systems in these areas, has caused the construction industry to begin developing practices that have less environmental impact. Innovative new materials and techniques will be largely governed by economic returns on this investment. Since many of the environmental goods affected by development are public in nature and rarely internalized by private firms, it is important to comprehensively evaluate each new practice so that there is a clear accounting of the costs and benefits to society as well as to private building owners.

This study evaluated one such innovative practice: the extensive green roof system. Applying a life-cycle BCA to this practice demonstrates that under current conditions, the NPV of traditional roofs is substantially less than the when green roofs are built in the Tanyard Branch watershed. This may not be surprising, however, due to the novelty of the technology and the unique conditions in the Tanyard Branch watershed which are not ideal for realizing all green roof benefits. Changing reasonable assumptions about this analysis shows that green roofs may be more cost effective than traditional roofs given changes in green roof construction costs, higher energy prices, or possibly inclusion of other watershed-specific benefits. If energy costs rise or stormwater protection becomes more of a public priority—both highly plausible possibilities—then green roofs become more economically attractive.

Green roofs can provide both private and public benefits and should be included as a potential tool in watershed management manuals for use in highly developed areas. Architects, stormwater professionals and watershed planners can only benefit from having more options to alleviate the environmental impacts of urbanization. An assortment of techniques allows for interested parties to use the practices most effective given their particular location, goals, and resource constraints. As areas continue to become more highly urbanized, reconciling development interests and environmental concerns is essential. The greater the number of practices available to accomplish this goal, the easier it will be to reconcile this future conflict between the built and natural environment.

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Matrix based fertilizers reduce nitrogen and phosphorus leaching in three soils

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Abstract

We compared the efficacy of matrix based fertilizers (MBFs) formulated to reduce NO_3^- , NH_4^+ , and total phosphorus (TP) leaching, with Osmocote[®] 14-14-14, a conventional commercial slow release fertilizer (SRF) and an unamended control in three different soil textures in a greenhouse column study. The MBFs covered a range of inorganic N and P in compounds that are relatively loosely bound (MBF 1) to more moderately bound (MBF 2) and more tightly bound compounds (MBF 3) mixed with $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ and with high ionic exchange compounds starch, chitosan and lignin. When N and P are released, the chemicals containing these nutrients in the MBF bind N and P to a $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ starch–chitosan–lignin matrix. One milligram (8000 spores) of *Glomus intradices* was added to all formulations to enhance nutrient uptake. In all three soil textures the SRF leachate contained a higher amount of NH_4^+ , NO_3^- and TP than leachate from all other fertilizers. In all three soils there were no consistent differences in the amount of NH_4^+ , NO_3^- and TP in the MBF leachates compared to the control leachate. Plants growing in soils receiving SRF had greater shoot, root and total biomass than all MBFs regardless of $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ or $\text{Fe}_2(\text{SO}_4)_3$ additions. Arbuscular mycorrhizal infection in plant roots did not consistently differ among plants growing in soil receiving SRF, MBFs and control treatments. Although the MBFs resulted in less plant growth in this experiment they may be applied to soils growing plants in areas that are at high risk for nutrient leaching to surface waters.

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1. Introduction

Nitrogen (N) and phosphorus (P) are the two soil nutrients that most often limit plant growth. When N and P fertilizers are added to the soil overall N and P use efficiency is low because only the soluble fraction of these nutrients can be taken up by plants (Vassilev and Vassileva, 2003). Land managers and home owners commonly apply soluble forms of N and P as inorganic fertilizers in quantities greater than plants can assimilate, leading to leaching and often surface and ground water contamination (Vitousek et al., 1997; David and Gentry, 2000; Edwards et al., 2000; Sharpley et al., 2000).

Transport of P from agricultural soils to surface waters has been linked to eutrophication in fresh water and estuaries (Bush and Austin, 2001; Broesch et al., 2001; Daniel et al., 1998). Nitrogen and P accumulation in fresh or brackish water can overstimulate the growth of algae creating conditions that interfere with the health and diversity of indigenous plant and animal populations (Tveite, 1994; Pohle et al., 1991). Nonpoint N sources were responsible for more than 90% of N inputs to more than half of the 86 rivers studied in United States. Nonpoint P sources contributed over 90% of the P in a third of these rivers. Along the coastline of the North Atlantic Ocean nonpoint sources of N are some 9-fold greater than inputs from wastewater treatment plants (Bricker et al., 1999). Eutrophication is also widespread and rapidly expanding in most temperate lake, stream and coastal ecosystems. The incidence of harmful algal blooms has dramatically increased in recent years (Bricker et al.,

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1999). This increase is linked to eutrophication and other factors, such as changes in food webs that may increase decomposition and nutrient recycling or reduce populations of algae-grazing fish.

Fertilizer regimens could greatly benefit from more effective time release technologies that can better protect surface and ground water. We developed matrix based fertilizers (MBFs) that may reduce NH_4 , NO_3 and total P (TP) leaching. The MBFs cover a range of inorganic N and P in compounds that are relatively loosely bound (MBF 1) to more moderately bound (MBF 2) and more tightly bound compounds (MBF 3) mixed with $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ and with the high ionic exchange compounds starch, chitosan and lignin. We added *Glomus interadices*, a species of arbuscular mycorrhizal fungal spores that will form mycorrhizae in high nutrient environments, in the MBF formulations to increase plant nutrient uptake. Our objective was to determine if MBFs combined with arbuscular mycorrhizae would reduce N and P leaching compared to a slow release fertilizer (SRF) in sand, sandy loam and loam textured soils in a greenhouse column study.

2. Materials and methods

2.1. Fertilizer treatments

The MBF formulations in our study cover a range of common inorganic nutrient compounds combined with $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$. Starch, chitosan and lignin were chosen because of their high concentration of ionic exchange sites and their decomposition characteristics. Nutrients bound to the $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ starch-chitosan-lignin matrix become increasingly available to plants as the organic components in the matrix

degrade. The organic components in the matrix should degrade starch > chitosan > lignin in the order of more to less rapid. The matrix based formulations can be made to bind inorganic nutrients relatively loosely (MBF 1) to more tightly (MBF 3) by increasing the concentration of $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ and by varying the amounts of starch, chitosan and lignin in the matrix. When the matrix is applied to soil the soil microorganisms will degrade the starch in the matrix comparatively rapidly while chitosan will degrade less rapidly. Lignin is expected to degrade the slowest and should retain most of its ionic exchange sites for a longer time in most soil environments.

The MBF formulations are comprised of inorganic chemicals combined with starch, chitosan and lignin (Sigma, St. Louis, MO). Treatment 1 was a control; no fertilizer was applied to the columns (Table 1). Treatment 2 was 5.0 g of the Osmocote® (14-14-14) SRF which was equal to $345\text{ }\mu\text{g N}$ and $344\text{ }\mu\text{g P}$ per column and $167.7\text{ kg N ha}^{-1}$ and $166.9\text{ kg P ha}^{-1}$ (Table 1). Osmocote® (14-14-14) has a 3–4 month nutrient release pattern at 70°C . Treatment 3 was MBF 1 which received $313.0\text{ }\mu\text{g N}$ and $164.0\text{ }\mu\text{g P}$ per column and was equal to 152 kg N ha^{-1} and 80 kg P ha^{-1} . Treatment 4 was MBF 2 which received $249\text{ }\mu\text{g N}$ and $181\text{ }\mu\text{g P}$ per column and was equal to 121 kg N ha^{-1} and 88 kg P ha^{-1} . Treatment 5 was MBF 3 which received $60\text{ }\mu\text{g N}$ and $294\text{ }\mu\text{g P}$ per column and was equal to 29 kg N ha^{-1} and 143 kg P ha^{-1} . We added treatments 6–8 to determine the effect of $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3$ on N and P leaching in the columns. Treatment 6 was MBF 3 + Al – Fe which MBF 3 was placed over $0.488\text{ g Al}(\text{SO}_4)_3\text{H}_2\text{O}$ without $\text{Fe}_2(\text{SO}_4)_3$. MBF 3 + Al – Fe received $60.0\text{ }\mu\text{g N}$ and $294.0\text{ }\mu\text{g P}$ per column and was equal to 29 kg N ha^{-1} and 143 kg P ha^{-1} . Treatment 7 was MBF 3 – Al + Fe placed over $1.600\text{ g Fe}_2(\text{SO}_4)_3$ without $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$. MBF 3 – Al + Fe

Table 1
Chemical compounds used to comprise three different matrix based fertilizers in mg N and P in each column^a

Treatment Compound	1 CONT	2 SRF	3 MBF 1	4 MBF 2	5 MBF 3	6 MBF 3 + Al – Fe	7 MBF 3 – Al + Fe	8 MBF 3 – Al + Fe
NH_4NO_3	0.000	0.210	0.000	0.000	0.000	0.000	0.000	0.000
P_2O_5	0.000	0.200	0.000	0.000	0.000	0.000	0.000	0.000
K_2O	0.000	0.180	0.180	0.180	0.180	0.180	0.180	0.180
$\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$	0.000	0.000	0.472	0.472	0.236	0.236	0.236	0.236
$\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$	0.000	0.000	0.750	0.750	0.000	0.000	0.000	0.000
$\text{NH}_4(\text{H}_2\text{PO}_4)$	0.000	0.000	0.230	0.230	0.115	0.115	0.115	0.115
$\text{Ca}(\text{H}_2\text{PO}_4)_2$	0.000	0.000	0.468	0.468	0.234	0.234	0.234	0.234
$\text{Fe}(\text{P}_2\text{O}_7)$	0.000	0.000	0.334	0.334	1.490	1.490	1.490	1.490
$\text{Al}(\text{PO}_4)_3$	0.000	0.000	0.360	0.360	0.000	0.000	0.000	0.000
$\text{Al}(\text{SO}_4)_3\cdot \text{H}_2\text{O}$	0.000	0.000	0.488	0.366	0.000	0.488	0.000	0.000
$\text{Fe}_2(\text{SO}_4)_3$	0.000	0.000	0.400	0.800	1.600	0.000	1.600	0.000
Starch	0.000	0.000	1.000	1.000	1.000	1.000	1.000	1.000
Chitosan	0.000	0.000	1.000	1.000	1.000	1.000	1.000	1.000
Lignin	0.000	0.000	1.000	1.000	1.000	1.000	1.000	1.000

^a(mg compound in each column) MBF 1 is matrix based fertilizer formulation 1 = 152 kg N ha^{-1} and 80 kg P ha^{-1} ; MBF 2 is matrix based fertilizer formulation 2 = 121 kg N ha^{-1} and 88 kg P ha^{-1} ; MBF 3 is matrix based fertilizer formulation 3 = 29 kg N ha^{-1} and 143 kg P ha^{-1} . SRF = slow release fertilizer 5.0 g of Osmocote® (14-14-14) which includes NH_4NO_3 , P_2O_5 and K_2O .

received $60.0 \mu\text{g N}$ and $294.0 \mu\text{g P}$ per column and was equal to 29 kg N ha^{-1} and 143 kg P ha^{-1} . Treatment 8 was MBF 3 – Al – Fe MBF 3 – Al + Fe which was MBF 3 without $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ or $\text{Fe}_2(\text{SO}_4)_3$ which received $60.0 \mu\text{g N}$ and $294.0 \mu\text{g P}$ per column and was equal to 29 kg N ha^{-1} and 143 kg P ha^{-1} . We added the 8000 spores of *G. interadices* in 1.00 ml of reverse osmosis water to all MBF treatments (per column) to increase plant nutrient uptake.

2.2. Column description

A 2.0 mm wire screen was cut into squares ($125 \times 125 \text{ mm}$) and secured to the bottom of each 10.0 cm diameter $\times$ 30 cm long polyvinyl chloride cylinder (Fig. 1). A 14 cm diameter funnel was placed below each column in the rack and secured. Three kilograms of soil were placed in each column (columns were filled to 25 cm) leaving a 5 cm space at the top of each column. Soil in columns was loosely packed and then repeatedly washed with reverse osmosis water to flush nutrients that could be loosely held to soil particles. Columns were allowed to

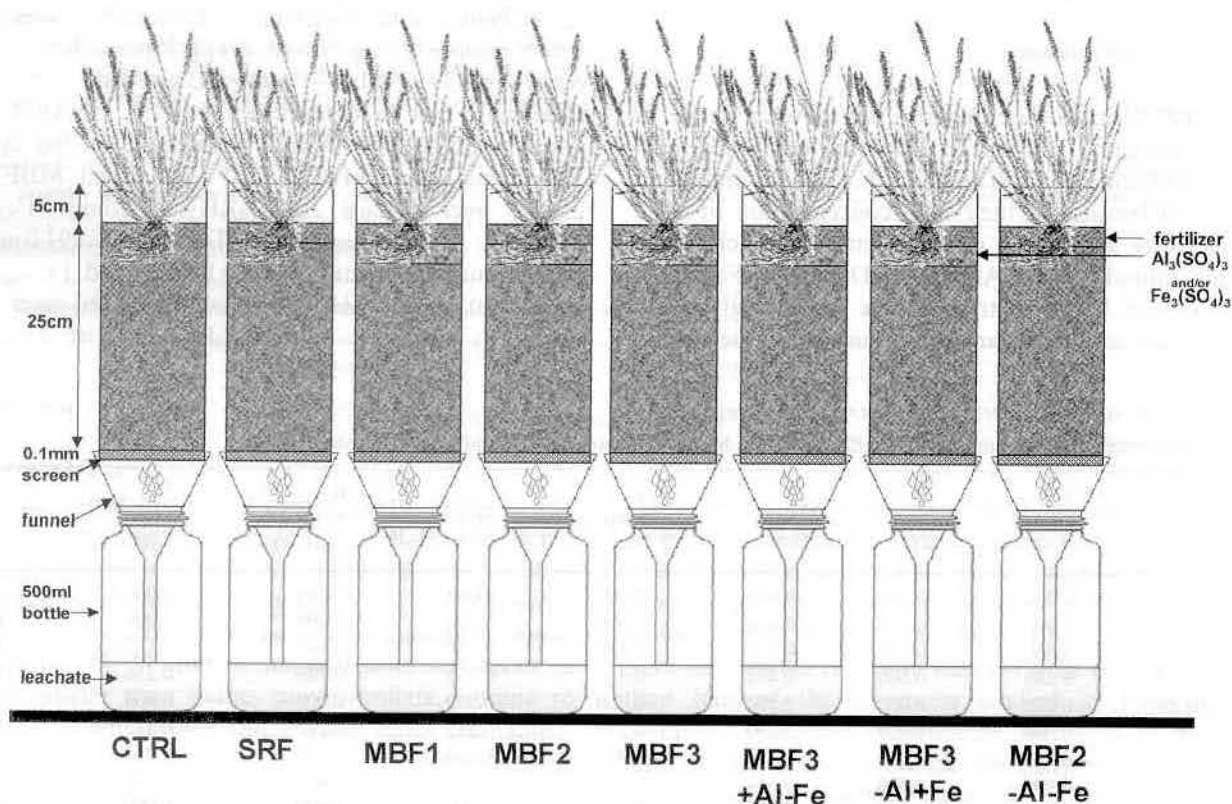
drain for 1 h prior to the start of leachate collection as described below.

2.3. Soil descriptions

Soils having three different textures were used to determine the effectiveness of the fertilizers to reduce leaching over a range of soil types. The Brown's Creek soil was a loam and was classified as a fine, montmorillonitic, mesic Xerollic Haplargid. The Simco soil was a coarse-loamy sand and classified as a mixed non-acid, mesic Xeric Torriorthents. The Kuna soil is a sandy loam and classified as a mixed, mesic lithic Xerollic Camborthids (Collett, 1982). Soil physical and microbiological properties are presented in Entry et al. (2002, 2004). Soil chemical concentrations are presented in Table 2.

2.4. Experimental design

The experiment was arranged in a completely randomized design (Kirk, 1982) with eight fertilizer treatments $\times$ three soil textures with three replications. There were a



CTRL = control which is column without fertilizer applied. SRF = slow release fertilizer which received $345 \mu\text{g N}$ and $344 \mu\text{g P}$. MBF1 = matrix based fertilizer 1 which received $313 \mu\text{g N}$ and $164 \mu\text{g P}$. MBF2 = matrix based fertilizer 2 which received $249 \mu\text{g N}$ and $181 \mu\text{g P}$. MBF3 = matrix based fertilizer 3 which received $60 \mu\text{g N}$ and $294 \mu\text{g P}$. MBF3 +Al-Fe = matrix based fertilizer 3 which received $60 \mu\text{g N}$ and $294 \mu\text{g P}$. MBF3 -Al+Fe = matrix based fertilizer 3 which received $60 \mu\text{g N}$ and $294 \mu\text{g P}$. MBF2 -Al-Fe = matrix based fertilizer 2 which received $249 \mu\text{g N}$ and $181 \mu\text{g P}$.

Fig. 1. Diagram of column apparatus. Treatment 1 was a control; no fertilizer applied to the column (CONT). Treatment 2 was a slow release fertilizer (SRF). Treatment 3 was matrix based fertilizer formulation 1 (MBF 1). Treatment 4 was matrix based fertilizer formulation 2 (MBF 2). Treatment 5 was matrix based fertilizer formulation 3 (MBF 3). Treatment 6 was matrix based fertilizer 3 without $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and without $\text{Fe}_2(\text{SO}_4)_3$ (MBF 3 + Al – Fe). Treatment 7 was matrix based fertilizer formulation 3 with $0.488 \text{ g Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and without $\text{Fe}_2(\text{SO}_4)_3$ (MBF 3 – Al – Fe). Treatment 8 was matrix based fertilizer formulation 3 without $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3$ (MBF 3 – Al – Fe).

Table 2

Extractable nutrient concentration in a loam, sand, and loamy sand soils^a

Soil	C	N	P	Fe	Mn	S	Si	Al	Zn
	(g C kg ⁻¹ soil)	(mg element kg ⁻¹ soil)							
Loam	0.47 b	8300 a	1440 a	250 a	22 b	728 a	470 a	14 a	8.7 a
Sandy Loam	0.69 a	5900 b	861 b	120 b	35 a	462 b	329 a	5 b	7.6 a
Sand	0.28 c	6500 b	846 b	150 b	15 c	759 a	411 a	8 b	11.3 a

^aIn each column and soil, values followed by the same letter are not significantly different as determined by the least-square means test ($p \leq 0.05$, $n = 3$).

total of 72 columns and 360 leachate measurements. Plants were given 100 ml reverse osmosis water each day for 16 weeks. Samples were measured for NH_4 , NO_3 , and TP in leachate at 21, 42, 63, 84 and 112 days.

2.5. Fertilizer placement and growing conditions

We placed the above stated amounts of $\text{Fe}_2(\text{SO}_4)_3$ and/or $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ at a depth of 5 cm in columns receiving MBF treatments 6–8. The MBF formulations were placed directly above the $\text{Fe}_2(\text{SO}_4)_3$ and/or $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$. The slow release Osmocote[®] 14-14-14 fertilizer not receiving additional $\text{Fe}_2(\text{SO}_4)_3$ and/or $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ was mixed into the top 5 cm of soil. We then placed 0.5 g of white soft spring wheat (*Triticum aestivum* L.cv. Frame) seed on top of each column. Seeds were covered with 0.5 cm of soil. Seeds were watered with 100 ml of water daily to maintain field capacity of the soil. Leachate did not flow through columns when 100 ml water was applied. We collected leachate 21, 42, 63, 84 and 112 days after fertilizer placement (start of the experiment) by giving plants 500 ml reverse osmosis water on the above stated days in lieu of the 100 ml daily reverse osmosis water. On each sampling day approximately 200 ml leachate was collected from each column. Subsamples were analyzed for NO_3^- and NH_4^+ and TP as described below. Throughout the experiment plants were exposed to light having a photosynthetic active radiation of $400\text{--}700 \mu\text{mol m}^{-2} \text{ s}^{-1}$ and a 14–16 h photoperiod.

2.6. Harvesting and arbuscular mycorrhizae assessment

After 112 days, plants were removed from the columns and separated into roots and shoots. Roots were washed in reverse osmosis water until all visible soil particles were removed. Three g of roots were randomly selected from each plant and placed in a solution of 2.5% (w/v) KOH. The roots in the KOH solution were then placed in an autoclave for 5 min and then rinsed in 2% HCl for 24 h. Roots were then placed in 0.05% (w/v) trypan blue in acidic glycerol for 24 h (Koske and Gemma, 1989). Roots were observed for hyphal colonization under a $200\times$ microscope by the cross hair intersection method (McGonigle et al., 1990). Approximately 100 intersections were scored and used to determine percent of root length infected. Root tissue excluding roots examined for mycor-

rhizal infection and shoot tissue was dried at 80°C for 48 h and weighed for shoot and root biomass.

2.7. Chemical analysis

Nitrate and NH_4^+ were determined using a Lachat Automated Ion Analyzer (Quickchem 8000 Systems; Milwaukee, WI) using the method as described by Greenberg et al. (1992). Total P in leachate was determined by digesting 25 ml aliquots in an autoclave at 103.5 kPa and 121°C for 60 min with 4.0 ml acidified ammonium persulfate (Greenberg et al., 1992). Three soil samples from each soil type were dried at 65°C for 72 h and passed through a 2 mm sieve. Total C was estimated by dry ashing at 525°C and assuming C equal to 50% of loss on ignition (Nelson and Sommers, 1996). Total N was determined using standard microkjeldahl procedures modified for NO_3^- (Bremner, 1996). A 2 g subsample of soil was extracted with 10 ml 1 N ammonium acetate (Sims, 1989) and analyzed for Mn, Fe, Al, Si, S and Zn were determined using inductively coupled plasma emission spectrometry (ICP). At harvest, plant root and shoot material were weighed then ground to pass a 1 mm mesh. A 0.50 g subsample was analyzed for total N with a LECO CHN-600 nitrogen analyzer (St. Joseph, Michigan). A 0.25 g subsample was ashed at 500°C , dissolved in 25 ml of 1.0 M HCl, brought to 50 ml volume with reverse osmosis water and analyzed for P, K, Ca, Mg, Mn, Fe, Cu, B and Zn using a inductively coupled plasma emission spectrometer (Perkin-Elmer, Boston, MA).

2.8. Statistical analysis

Nitrate, NH_4^+ and TP values were tested for normal distribution. Data were then analyzed using general linear models (GLM) procedures for a completely random design with Statistical Analysis Systems (SAS Institute Inc., 1996). In all analyses, residuals were equally distributed with constant variances. Differences reported throughout are significant at $p \leq 0.05$, as determined by the least-squares means test.

3. Results

The GLM of leached nutrients for soil type $\times$ fertilizers $\times$ sample day, soil type $\times$ fertilizers, and soil

type $\times$ sample day were not significant, therefore, statistical comparisons of NH_4^+ , NO_3^- and total P are presented for fertilizer treatments because GLM showed these interactions were significant at $p \leq 0.05$ (Snedecor and Cochran, 1980).

After 112 days, SRF leachate contained a greater amount of NH_4^+ , NO_3^- and TP than leachate from all other fertilizers (Figs. 2–4). In all three soils, MBFs reduced NH_4^+ in leachate by a minimum of 50%, NO_3^- leachate by a minimum of 46% and TP in leachate by a minimum of 200%. In all three soils there were no consistent differences in the amount of NH_4^+ , NO_3^- and TP in the MBF leachates than in the control leachate. Plants growing in soils receiving SRF had greater head weight, shoot, root and total biomass than all fertilizer formulations (Table 3). All fertilizer formulations and SRF plants had greater head weight, shoot, root and total biomass than plants growing in soils receiving no fertilizer (control). Arbuscular mycorrhizal infection in plant roots did not consistently differ among plants growing in soil receiving SRF and all MBF formulations and plants growing in soils receiving no fertilizer (control). Plants growing in the loam soil receiving SRF treatment had greater shoot and root N concentrations than all MBF formulations except for the MBF 1 shoot N concentration. Plants growing in the sand and sandy loam soils receiving SRF treatment had greater shoot N concentrations than all

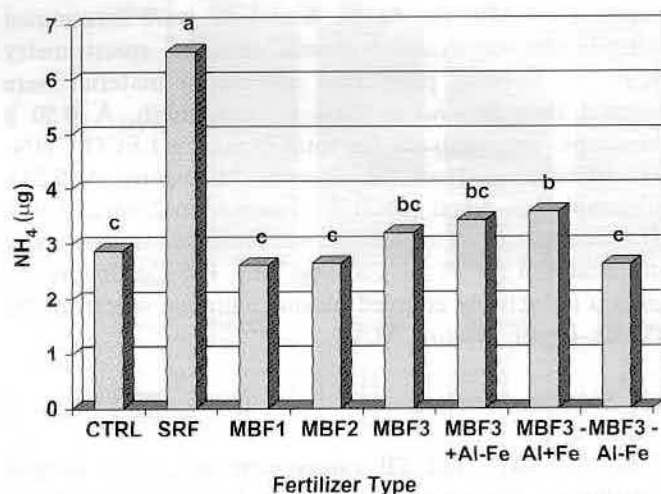


Fig. 2. Total amount of NH_4 leached from soil columns growing wheat over 112 days. Treatment 1 was a control; no fertilizer applied to the column (CONT). Treatment 2 was a slow release fertilizer (SRF). Treatment 3 was matrix based fertilizer formulation 1 (MBF 1). Treatment 4 was matrix based fertilizer formulation 2 (MBF 2). Treatment 5 was matrix based fertilizer formulation 3 (MBF 3). Treatment 6 was matrix based fertilizer 3 without $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and without $\text{Fe}_2(\text{SO}_4)_3$ (MBF 3 + Al – Fe). Treatment 7 was matrix based fertilizer formulation 3 with 0.488 g $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and without $\text{Fe}_2(\text{SO}_4)_3$ (MBF 3 – Al + Fe). Treatment 8 was matrix based fertilizer formulation 3 without $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3$ (MBF 3 – Al – Fe). Bars having same letter are not significantly different as determined by the least-square means test ($p \leq 0.05$), $n = 360$.

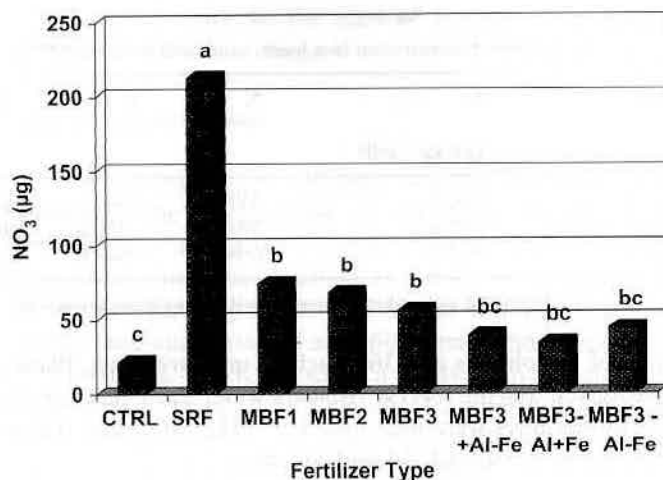


Fig. 3. Total amount of NO_3 leached from soil columns growing wheat over 112 days. Treatment 1 was a control; no fertilizer applied to the column (CONT). Treatment 2 was a slow release fertilizer (SRF). Treatment 3 was matrix based fertilizer formulation 1 (MBF 1). Treatment 4 was matrix based fertilizer formulation 2 (MBF 2). Treatment 5 was matrix based fertilizer formulation 3 (MBF 3). Treatment 6 was matrix based fertilizer 3 without $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and without $\text{Fe}_2(\text{SO}_4)_3$ (MBF 3 + Al – Fe). Treatment 7 was matrix based fertilizer formulation 3 with 0.488 g $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and without $\text{Fe}_2(\text{SO}_4)_3$ (MBF 3 – Al + Fe). Treatment 8 was matrix based fertilizer formulation 3 without $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3$ (MBF 3 – Al – Fe). Bars having same letter are not significantly different as determined by the least-square means test ($p \leq 0.05$), $n = 360$.

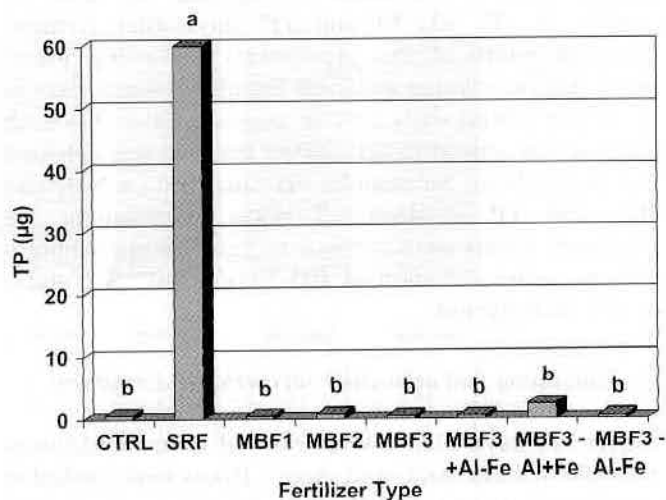


Fig. 4. Total amount of total phosphorus (TP) leached from soil columns growing wheat over 112 days. Treatment 1 was a control; no fertilizer applied to the column (CONT). Treatment 2 was a slow release fertilizer (SRF). Treatment 3 was matrix based fertilizer formulation 1 (MBF 1). Treatment 4 was matrix based fertilizer formulation 2 (MBF 2). Treatment 5 was matrix based fertilizer formulation 3 (MBF 3). Treatment 6 was matrix based fertilizer 3 without $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and without $\text{Fe}_2(\text{SO}_4)_3$ (MBF 3 + Al – Fe). Treatment 7 was matrix based fertilizer formulation 3 with 0.488 g $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and without $\text{Fe}_2(\text{SO}_4)_3$ (MBF 3 – Al + Fe). Treatment 8 was matrix based fertilizer formulation 3 without $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3$ (MBF 3 – Al – Fe). Bars having same letter are not significantly different as determined by the least square means test ($p \leq 0.05$), $n = 360$.

Table 3
Wheat height, biomass, and head weight after 112 days growth in a loam, sand, and loamy sand soil in greenhouse conditions^{a,b}

Soil	Treatment	Height	Head weight	Shoot biomass	Root biomass	Plant biomass	Mycorrhizal infection	Shoot N	Shoot P	Root N	Root P
		(cm)	(g)	(g)	(g)	(g)	(arbuscules/mm)	(mg kg ⁻¹)			
Loam	Control (no fertilizer)	44.0 c	6.5 c	11.5 d	12.7 c	24.2 c	3.7 b	8300 b	168.2 c	5333 b	3553 c
	SRF	49.0 b	17.2 a	26.9 a	29.5 a	56.4 a	40.9 a	16060 a	732.6 a	7833 a	8567 a
	MBF 1	57.9 a	12.6 b	21.8 b	24.0 b	40.0 b	20.6 a	10700 ab	278.2 b	5200 b	4123 bc
	MBF 2	57.6 a	12.6 b	21.0 b	23.1 b	44.2 b	27.7 a	8300 b	304.6 b	4300 b	3806 bc
	MBF 3	56.8 a	9.7 b	16.4 c	18.1 b	34.5 b	13.0 ab	7333 b	235.9 b	3933 b	4367 b
	MBF 3 + Al – Fe	54.3 a	9.4 b	16.2 c	17.8 b	33.9 b	15.6 ab	7633 b	282.7 b	4800 b	5373 b
	MBF 3 – Al + Fe	50.4 a	8.6 b	15.0 c	16.5 b	31.5 b	43.3 a	8467 b	221.0 b	4000 b	4123 bc
	MBF 2 – Al – Fe	55.9 a	11.7 b	19.2 bc	21.1 b	34.2 b	19.6 ab	8530 b	276.6 b	4333 b	4553 b
Sand	Control (no fertilizer)	24.8 b	0.8 c	1.7 c	1.9 c	3.6 c	16.9 a	5900 c	14.6 c	4800 b	3563 c
	SRF	51.9 a	17.3 a	28.0 a	30.9 a	58.9 a	20.3 a	13733 a	614.0 a	7800 a	6073 ab
	MBF 1	50.3 a	7.7 b	15.4 b	16.9 b	38.8 b	8.0 ab	8666 b	134.7 b	5800 b	6226 ab
	MBF 2	51.7 a	8.9 b	15.9 b	17.5 b	33.4 b	21.0 a	7566 b	197.4 b	4900 b	4280 b
	MBF 3	47.6 a	6.0 b	10.1 b	12.1 b	23.1 b	28.3 a	7033 b	153.7 b	4566 b	4120 bc
	MBF 3 + Al – Fe	51.4 a	6.4 b	11.7 b	12.8 b	24.5 b	6.1 b	7433 b	193.8 b	4200 b	5617 b
	MBF 3 – Al + Fe	47.1 a	6.9 b	12.4 b	13.7 b	26.1 b	5.1 b	7100 b	151.6 b	4833 b	3687 b
	MBF 2 – Al – Fe	52.7 a	8.6 b	16.3 b	17.9 b	34.2 b	20.9 a	7666 b	180.2 b	4500 b	3390 b
Sandy Loam	Control (no fertilizer)	39.5 b	2.8 c	5.9 c	6.4 c	12.4 c	26.3 a	6466 c	47.2 c	5400 b	3300 c
	SRF	48.0 a	18.1 a	28.7 a	31.6 a	60.3 a	24.1 a	15833 a	586.9 a	7400 a	5806 a
	MBF 1	56.9 a	10.6 b	20.0 b	22.0 b	41.9 b	35.2 a	7166 b	194.8 b	5100 b	3912 bc
	MBF 2	54.0 a	10.3 b	18.4 b	20.3 b	38.7 b	15.4 a	8300 b	257.8 b	4066 b	5247 b
	MBF 3	53.0 a	9.6 b	17.8 b	19.5 b	37.3 b	17.6 a	7600 b	210.7 b	4133 b	4346 b
	MBF 3 + Al – Fe	52.0 a	9.1 b	16.5 b	18.1 b	34.6 b	24.3 a	9500 b	191.6 b	3900 b	5246 b
	MBF 3 – Al + Fe	50.9 a	8.7 b	16.3 b	17.9 b	34.2 b	29.6 a	9833 b	161.2 b	4800 b	5183 b
	MBF 2 – Al – Fe	50.1 a	8.9 b	16.2 b	17.8 b	34.0 b	26.3 a	7566 b	182.5 b	4133 b	4057 b

^aIn each column and soil, values followed by the same letter are not significantly different as determined by the least-square means test ($p \leq 0.05$, $n = 9$).

^bMBF 1 is matrix based fertilizer formulation 1 = 152 kg N ha⁻¹ and 80 kg P ha⁻¹; MBF 2 is matrix based fertilizer formulation 2 = 121 kg N ha⁻¹ and 88 kg P ha⁻¹; MBF 3 is matrix based fertilizer formulation 3 = 29 kg N ha⁻¹ and 143 kg P ha⁻¹.

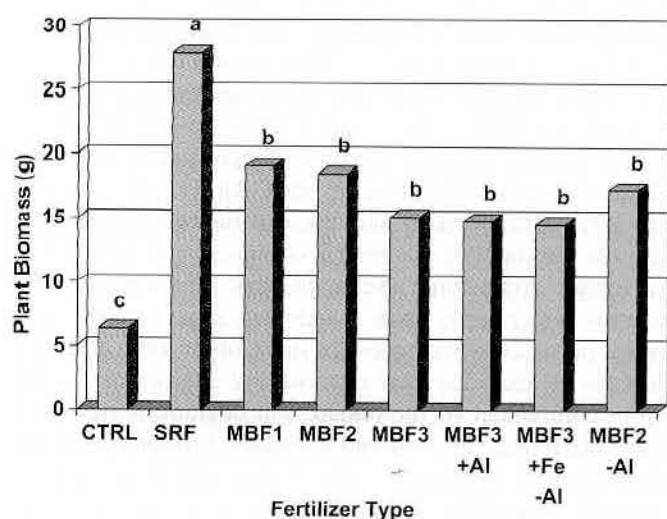


Fig. 5. Total amount of plant biomass from soil columns growing wheat over 112 days.

MBF formulations. Plants growing in soils receiving SRF had greater shoot P content than all MBF formulations. All fertilizer and SRF plants had greater shoot P content than plants growing in soils receiving no fertilizer (control). The concentration of K, Ca, Mg, Mn, Fe, Cu, B and Zn in root and shoot tissue did not differ ($p \leq 0.05$) among treatments (data not shown) (Fig. 5, Table 2).

4. Discussion

We found that 70–86% of the NH_4^+ , 75–84% of the NO_3^- and 84% of the total P was leached from the soil columns in the first 63 days after the Osmocote[®] (14-14-14) SRF was applied (data not shown). Plants growing in soils receiving SRF had greater plant biomass (growth) shoot and root N and P content than all MBF formulations regardless of $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ or $\text{Fe}_2(\text{SO}_4)_3$ additions. Plants growing in soils receiving SRF had 15–55% greater plant biomass than those growing in MBF formulations 112 days after application. The growth rate of plants in soils receiving SRF was greater than those growing in soil receiving MBF formulations in the 112 day time period, presumably because in soils receiving SRF, the nutrients were more available to the plant. Shoot biomass, shoot N and P, and head weight were greater in plants given SRF than the MBF formulations. The MBF formulations contained more N and P than the SRF, but a significant amount of the nutrients were bound to the $\text{Al}(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, or $\text{Fe}_2(\text{SO}_4)_3$, starch, chitosan and lignin exchange matrix and more slowly available to plants. A small fraction of N and P is probably immobilized in the matrix and only available to plants over months or years. Future studies should include a fertilizer rate study to determine the amount of the MBFs that can be applied to soils to increase plant growth equal to plant growth obtained by

fertilization with the SRF while still reducing N and P leaching.

Direct losses of P from fertilizer leaching or runoff usually result when fertilizer application is coincident with heavy rain events (Haygarth and Jarvis, 1999). We found 84% of the total P was leached from these columns in the first 43 days after treatments commenced. Our results imply that, even if the SRFs available on the market today were applied at rates to meet crop or turf P nutrition over a growing season and plants grew at their maximum potential, it would be difficult for them to take up a sufficient amount of fertilizer P to prevent leaching. Therefore, even if agricultural and turfgrass operators were to apply nutrients in amounts anticipated to meet plant requirements over the growing season, substantial amounts of N and P could be leached. The problem is made more severe because some turfgrass operators and homeowners often apply nutrients in quantities exceeding plant requirements (Hart et al., 2003). Several studies indicated that sediment bound P concentrations in runoff generally increase as soil P concentrations increase (Sharpley et al., 1993; Pote et al., 1999; Cox and Hendricks, 2000). Long-term overfertilization of soils is recognized as potentially contributing to eutrophication of surface waters (Sims, 1993; Frossard et al., 2000).

Conventional fertilizers formulations such as single super phosphate (SSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP) were developed with the goal of minimizing the production costs per unit of soluble P. The study of SSP, MAP and DAP modification to reduce susceptibility to P runoff and leaching has been limited (Hart et al., 2003). SRFs have been employed to reduce direct fertilizer runoff losses. Nutrient leaching from SRFs is reduced through degradation of an organic or inorganic coating around a core of inorganic fertilizer. Quin et al. (2003) describe coating a DAP with a slurry of elemental sulfur which provides a short-term barrier to water. Field trials demonstrated an approximately 40% reduction of P runoff during the first runoff event after application. Nash et al. (2003) conducted laboratory dissolution studies comparing SSP and a dry sulfur-coated superphosphate, in which sulfate of ammonia was the binding agent. The authors found that the water-extractable P was greater from the coated superphosphate fertilizer treatments (6.6%) compared to 4.8% from superphosphate treatments. The rapid dissolution of the S-coated superphosphate resulted from the rapid solubilization of the sulfate of ammonia in the extraction procedure, and with it removal of the sulfur coat and protection against P dissolution in the granules (Hart et al., 2004).

Commercial SRFs can be classified into two basic groups: low solubility and polymer coated water soluble fertilizers (Blaylock et al., 2005). The polymer coated SRFs are water soluble and can exhibit consistent nutrient release rates. However, average soil temperature and moisture need to be known. The fertilizers are characterized by one

or more polymeric resins surrounding the fertilizer. The duration of nutrient release is controlled by the porosity of the resin coating. A more porous coating results in quicker release. When polymer coated SRFs are applied to the soil, the water in the soil enters the fertilizer granule through micropores which dissolves the nutrients. Nutrients are then steadily released through the pores. The rates of nutrient release of polymer coated SRFs are influenced by soil temperature, the higher the soil temperature, the greater the release rate (Blaylock et al., 2005). Release rate is hypothesized to be not significantly influenced by microbiological decomposition, soil moisture, soil type or pH. However, all polymers eventually degrade in soil (Basfar et al., 2003; Bonhomme et al., 2003; Lehmann et al., 2000, 1998) and the degradation rate influences nutrient release from the polymer.

The MBF formulations in our study cover a range of common inorganic nutrient compounds combined with $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ and the high ionic exchange compounds starch, chitosan and lignin. These formulations allow nutrients to bind with the $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ -lignin-chitosan matrix substantially reducing leaching (Entry and Sojka, 2007). Nutrient ions having become bound to the $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ -lignin-chitosan matrix will slowly become available to most plants over several growing seasons. These matrix based formulations cover a range of inorganic N and P in compounds that are relatively loosely bound (MBF 1) to more moderately bound (MBF 2) and more tightly bound compounds (MBF 3) mixed with $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ and with the high ionic exchange compounds starch, chitosan and lignin. When N and P are released from the chemicals containing these nutrients the MBFs likely bind N and P to a $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ starch-chitosan-lignin matrix. After the starch-chitosan-lignin matrix with $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ is applied to soil the soil microorganisms will degrade the starch in the matrix comparatively rapidly and will create some ionic exchange sites. The chitosan will degrade less rapidly than starch but more rapidly than lignin and is expected to retain most of its ionic exchange sites for at least one year in most soil environments. The lignin component in the matrix will degrade more slowly than starch and chitosan and is expected to retain its ionic exchange sites for several years in most soil environments. Nutrient availability and leaching is expected to be controlled to a large degree by varying the relative amounts of starch-chitosan-lignin matrix with $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ in the mixture. The MBFs bind nutrients to the $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$ starch-chitosan-lignin matrix and application rates are based on the amount of nutrients released to meet plant growth, therefore their application rates will necessarily not be comparable to conventional or SRFs, which release nutrients based on the amount of nutrient applied.

Mycorrhizal colonization in plant roots did not differ among SRF, MBF 1, MBF 2 and MBF 3 formulations

with or without $\text{Al}(\text{SO}_4)_3\text{H}_2\text{O}$ and/or $\text{Fe}_2(\text{SO}_4)_3$. Mycorrhizal colonization was assessed at the termination of the experiment when roots were growing throughout the soil. The mycorrhizal associations with *G. interadicius* probably formed in the first few weeks of the experiment and subsequently, as roots grew and suberized, the colonizations at that location in the root diminished. *G. interadicius* is an arbuscular mycorrhizal fungi species that will form associations with a broad range of host plants in soils containing high concentrations of nitrogen and phosphorus. *G. interadicius* was added to the matrix to enhance plant uptake of N and P.

The impact of MBF to reduce N and P leaching in the field may not be readily apparent in most cases, especially in agricultural soils. Fertilization on the same soils for years will result in N and P sorption on clay and organic matter ionic exchange sites (D'Angelo, 2005; McDowell et al., 2005; Bird et al., 2002, 2003; Devere and Horwath, 2001). Fertilizer N and P will also have become incorporated into organic matter complexes which will result in these nutrients being released as organic matter is decomposed (Bird et al., 2003, 2002; Entry and Emmingham, 1995). The efficacy of MBF to reduce N and P input to surface and ground water should be more apparent on highly leached sandy soils than soils containing high concentrations of silt, clay or organic matter. The use of ^{15}N and ^{31}P labeled chemical components in MBF may be the most accurate method to determine the quantities of these nutrients leached from the fertilizer in most soils.

5. Conclusions

These new fertilizer formulations do not depend on organic or inorganic coatings to reduce N and P leaching and with further testing and development could be more effective than commercial fertilizers. Although further greenhouse and field testing are called for, results of this initial investigation are promising. Cost estimates of these MBF has been calculated to be $\$0.03\text{--}0.08\text{ kg}^{-1}$ above the cost of conventional fertilizers. One of the main goals of future research should be to reduce the cost of MBF production. MBFs initially may be economically feasible for use by homeowners on their lawns, turfgrass operators such as golf course managers and growers of high value agricultural crops. The MBF formulations could prove important in soils whose water flow drains into nutrient-affected waters such as Chesapeake Bay, Florida Everglades and rivers flowing into the Great Lakes.

As nutrients are applied to a soil they can accumulate to the maximum retention capacity of the soil, which is controlled by soil physical and chemical properties, the resident biota and the rate of nutrient uptake by vegetation. Continual excessive application of any fertilizer eventually will load soil beyond its maximum retention capacity. Nutrients added to the soil above that limit via any mode of application (e.g. natural and anthropogenic aerial deposition, application of fertilizer) eventually can be

released to water flowing over and/or through the soil. Improved technology cannot substitute fully for adhering to sound land management practices. In the long-term N and P contamination of water can be prevented only by applying nutrients in quantities relative to the inherent capacity of the soil to retain nutrients and the quantities removed via harvest. However, new MBF formulations that release nutrients at a rate comparable to plant uptake can reduce nutrient leaching and ultimately eutrophication.

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Coupling a 3D patch model and a rockfall module to assess rockfall protection in mountain forests

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Abstract

Many forests in the Alps are acknowledged for protecting objects, such as (rail) roads, against rockfall. However, there is a lack of knowledge on efficient silvicultural strategies and interventions to maintain these forests at optimal protection level. Therefore, assessment tools are required that quantify the rockfall protection effect of forest stands over time, and thereby provide the ability to evaluate the necessity and effect of management interventions. This paper introduces such a tool that consists of a 3D rockfall module embedded in the patch based forest simulator PICUS. The latter is extended for this study with a new regeneration module. In a series of experiments the new combined simulation tool is evaluated with regard to parameter sensitivity, model intercomparison experiments with recently proposed algorithms from the literature, and the ability to respond realistically to different management regimes in rockfall protection forests. Results confirm the potential of the new tool for realistic simulation of rockfall activity in heterogeneous mountain forests, but point at the urgent need to improve the knowledge base on the interaction of understory and rockfall activity. Further work will focus on model validation against empirical rockfall data, and include reduced tree vitality due to damage from boulder collisions as well as the explicit consideration of downed dead wood.

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1. Introduction

A particularly important function of forests in the Alps is to provide protection against natural hazards such as snow avalanches, debris flows and rockfalls. Therefore, many forest stands in the Alps have, next to a site-protection function in which forest cover stabilizes the slope itself, an object-protection function, which means that forest cover can protect objects and infrastructure

located further down a slope from natural hazards (Motta and Haudemand, 2000). Taking into account the increasing pressure from emerging tourism and increasing infrastructure needs in the Alps (Kräuchi et al., 2000), the object-protection function of mountain forests in Central Europe will only gain importance in future. However, there is a lack of knowledge on efficient silvicultural strategies and interventions to maintain protection forest structures, i.e. how to best overcome periods of decreased protection which may occur in managed stands as well as during natural forest development (Dorren et al., 2004; Perret et al., 2004). In the near future, such development is expectable on a large scale, as for instance in Austria, many protection forest stands enter their old growth phase and regeneration is in many cases lacking (BFW, 2004).

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Efficient management is most needed, while low productivity, difficult terrain and therefore high harvesting costs are often keeping owners and managers from intervening in protection forest stands.

In the current study focus will be on protection function of mountain forests against rockfall. Rockfall is defined here as a quick gravitational movement of rock boulders, rolling, tumbling or sliding down a hillslope (Selby, 1995). The boulders rather act independently and rockfall total mass lies typically below 5 m³ (Berger et al., 2002). Since interest in this study is on sustainable forest resource management, sufficient tools are needed that quantify the rockfall protective effect of forest cover over time, and thereby provide the ability to evaluate the necessity and effect of management interventions. Among the first attempts to characterise and quantify the protection effect of forest cover against rockfall are studies done by Jahn (1988), Gsteiger (1989) and Zinggeler (1989). While Jahn (1988) analysed empirical rockfall experiments while releasing boulders down a slope, Zinggeler (1989) mathematically analysed data sets of rockfall trajectories and thereby proved the influence of slope relief, soil condition and standing trees on the rockfall trajectory. In addition, Gsteiger (1989) developed the now widely applied, tested and adapted concept of the “mean tree free distance” or “average distance between contacts” (e.g., Gsteiger, 1993; Brauner et al., 2005; Dorren et al., 2005), which indicates the mean distance between two collisions of boulders with trees, or in other words: how often, on average, a boulder dissipates its energy by impacting a tree on its way down the slope.

The above-mentioned studies prove that an increasing amount of quantitative knowledge is available on the relation between the process of rockfall and forest structures in the Alps. Several assumptions on ideal forest structures have been tested in experimental studies, following Jahn (1988); e.g. Perret et al. (2004) and Dorren et al. (2005). In contrast, knowledge regarding the temporal relation between forest management interventions and rockfall is lacking (Dorren, 2002). Decision support tools are called for, which can predict this dynamic relation in a plausible manner (Dorren, 2002; Dorren et al., 2004; Kräuchi et al., 2000). Based on biomechanical considerations, Brauner et al. (2005) developed such a dynamic modelling tool for decision support in protection forest management. Two rockfall quantification models were coupled and implemented in an empirical distance-independent forest growth simulator. While the results of Brauner et al. (2005) are promising, there is still potential to improve the approach on spatial explicitness of both rockfall and forest vegetation simulation approaches. Similarly, Wehrli (2005) attempts to combine the forest gap model FORCLIM (Bugmann, 1996) and an existing rockfall simulation tool, and concludes that a spatially explicit representation of forest structure would enhance the approach.

Based on these considerations the objectives of this paper are:

- (1) the introduction of a new rockfall module, embedded in the patch-based forest simulator PICUS (e.g., Lexer and Hönninger, 2001). It is hypothesized that with this spatially explicit simulator the consequences of heterogenizing silvicultural interventions, typical for mountain forest management (Mayer and Ott, 1991; Ott et al., 1997; Pitterle, 1993), on rockfall protection can be considered with a higher level of accuracy and reliability;
- (2) the preliminary evaluation of the presented tool with regard to parameter sensitivity, comparison against model formulations from the literature with regard to key output variables, and the ability to respond realistically to different management regimes in rockfall protection forests.

2. Methods and material

2.1. The forest model PICUS v1.3

The model used in this study is the hybrid forest patch model PICUS v1.3 (Seidl et al., 2005), which incorporates elements of a classical patch model (PICUS v1.2, Lexer and Hönninger, 2001) as well as a stand level production model based on physiological principles (3-PG, Landsberg and Waring, 1997). The spatial structure of PICUS v1.2 (Lexer and Hönninger, 2001) is retained in the current model version. PICUS arranges tree biomass in space based on 10 × 10 m² patches with vertical resolution of 5 m. Within a patch the position of a tree is not known. A three-dimensional light model, allowing for explicit consideration of direct and diffuse radiation within the canopy, is used to model inter- and intra tree species competition. The incorporation of a production model that is based on the concept of radiation-use efficiency (Landsberg and Waring, 1997) enhanced accuracy in prediction of growth and yield. It also improved the physiological foundation of the model with regard to varying environmental conditions (Seidl et al., 2005). PICUS v1.3 requires input of incoming radiation, temperature, precipitation and vapour pressure deficit of the air in at least monthly resolution. The mortality submodel within PICUS follows the classical patch model approach (e.g., Keane et al., 2001) and has been complemented by a submodule of bark beetle induced mortality in *Picea abies* (L.) Karst. (Lexer, 2001). So far, regeneration in PICUS has been simulated with a recruitment submodel (e.g., Vancley, 1994; Price et al., 2001).

2.1.1. Extended regeneration submodel

For the realistic inclusion of a rockfall module in PICUS v1.3 the recruitment component required a major update since the regeneration layer plays an important role in the rockfall process. In designing the new regeneration module three core requirements had been set: (i) due to high

uncertainties in modelling mountain forest regeneration (e.g., Kindermann et al., 2002), the model structure was kept as simple as possible, (ii) biological processes were considered whenever possible, and (iii) key parameters as well as flow and state variables should be observable to allow model validation against empirical data. In the following section a brief outline of the new regeneration module within PICUS is given. For further details on model logic and structure we refer to Lexer and Hönninger (2001), Lexer (2001) and Seidl et al. (2005).

As in previous model versions, seeds produced by mature trees are distributed in the simulated forest mimicking zoochorous and anemochorous processes. According to the model concept the probability of regeneration establishment on a particular patch in a given year is calculated per species based on the available light on the forest floor, the stockable relative area per patch, and the effective number of seed of a species on a patch. A prerequisite for the new module was the enhancement of the light model within PICUS because in recent model versions trees had not been initialized explicitly below 1.3 m height, and subsequently were not considered in modelling light levels at the forest floor:

$$avL_{\text{floor}} = avL_{\text{bottom}} e^{-0.7 BM}, \quad (1)$$

where avL_{floor} is the relative available light at the forest floor incl. regeneration ≤ 130 cm [0–1], avL_{bottom} the relative available light in the lowest crown cell (without regeneration ≤ 130 cm) [0–1], 'e' the base of natural logarithm, and BM the aboveground dry mass of regeneration ≤ 130 cm [kg m^{-2}].

Eq. (2) estimates the probability of establishment in a given year, per patch and per species. $S_{\text{eff}(ij)}$ is the seed of a

species (j) on patch (i) after applying the species-specific germination rate and the environmental filters of the temperature regime, soil moisture and nutrient supply (see Lexer and Hönninger, 2001):

$$P(\text{est})_{ij} = (1 - e^{(-a S_{\text{eff}(ij)} SA(i) L_{\text{resp}(ij)})})^{(1 - L_{\text{resp}(ij)})}, \quad (2)$$

$P(\text{est})_{ij}$ is the probability of establishment for species (j) on patch (i) [0–1], $S_{\text{eff}(ij)}$ the effective number of seed of species(j) at patch(i) [nm^{-2}], $SA(i)$ the proportion of stockable area of patch(i) [0–1], $L_{\text{resp}(ij)}$ the light response of species (j) at patch (i) on forest floor [0–1], and a the empirical coefficient.

The coefficient a can be estimated from field data. In the current study it was set to 0.0005. The rationale was that based on explorative simulation experiments under unlimited seed supply the model produced realistic results with regard to number of seedlings along both a site and light gradient which could be confirmed by qualitative literature data (Ruhm, 2004; Müller, 2003). A random number decides whether new individuals of a species are added to the lowest of four height classes ($H_1 = 0–10$ cm, $H_2 = 10–30$ cm, $H_3 = 30–80$ cm, $H_4 = 80–130$ cm). Growth of established seedlings is modelled within that size-class frame. Per size-class a representative individual is defined. Currently, all conifers and all broadleaf species respectively are pooled. The relationship of dry mass and height of individual seedlings shown in Fig. 1 is used to calculate BM in Eq. (1).

A species-specific height growth potential per height class is modified with the light response of the species as a process-based proxy of competition by vegetation of the same height or taller as the target height class to get an estimate of actual height growth $ih_{\text{sim}(ijk)}$ (Eq. (3a)). The

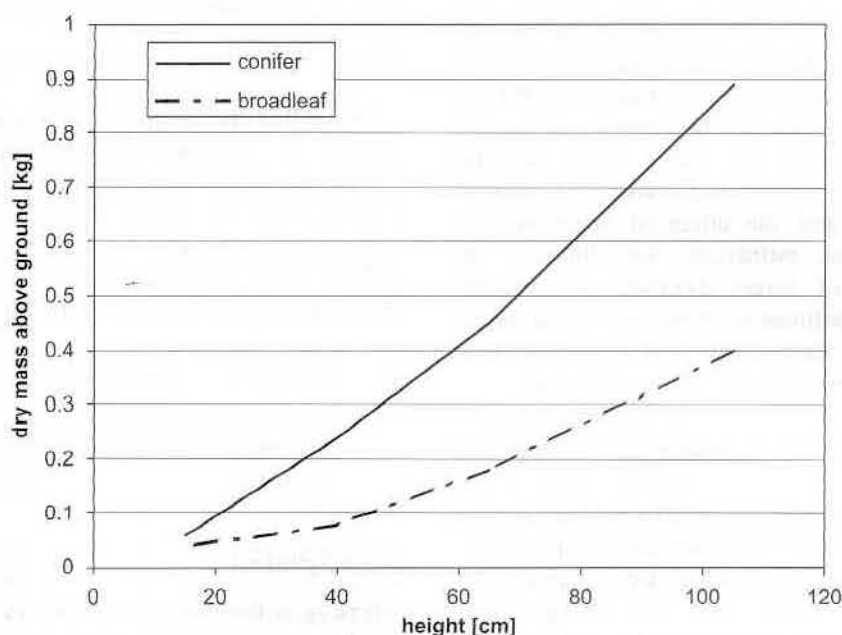


Fig. 1. Relationship of dry mass of aboveground biomass and height for pooled conifer and broadleaf seedlings (Hochbichler, unpublished data).

number of individuals per species (j) growing from height class (H_k) into height class (H_{k+1}) is calculated with Eq. (3b):

$$ih_{sim(ijk)} = ih_{pot(ijk)} L_{resp(ijk)}, \quad (3a)$$

$$A_{ijk} = n_{ijk} \frac{ih_{sim(ijk)}}{b}, \quad (3b)$$

where A_{ij} is the number of individuals of species (j) at patch (i) growing from $H(k)$ to $H(k+1)$ [$\text{m ha}^{-1} \text{yr}^{-1}$], n_{ijk} the stem number of species (j) at patch (i) in $H(k)$ [m ha^{-1}], $ih_{pot(ijk)}$ the potential annual height growth of species (j) in $H(k)$ [cm yr^{-1}], $L_{resp(ijk)}$ the light response of species (i) at patch (j) in height class (k) [0–1], $ih_{sim(ijk)}$ the actual height growth of species (j) at patch (i) in height class (k) [cm yr^{-1}], and b the width of $H(k)$ [cm].

If a species fails to achieve a minimum height growth for a specified number of successive years a percentage of individuals per height class dies. Outgrowth from H_4 is initialized as individual trees within the PICUS simulation environment. Further growth, seed production and mortality are then simulated as described in Seidl et al. (2005).

2.2. The rockfall submodule

2.2.1. General layout

In PICUS, the initial forest conditions regarding the distribution of trees can be established by (i) randomly allocating the trees of a population over the patches, or (ii) manually allocating each tree individually to a particular patch. By the latter approach any forest structure can be realized within the 100 m^2 resolution of the patch array. Gaps can be simulated by leaving patches out of the tree distribution. Once allocated to a patch, the trees are randomly assigned a position within the patch considering minimum neighbourhood distances. This feature was included to specifically address the needs of the rockfall module. However, for simulating forest dynamics the patch is still the basic spatial modelling entity. Currently, PICUS v1.3 simulates forest dynamics on a horizontal patch array. For the rockfall simulation the patch array is tilted according to slope. Every simulated year the rockfall module can be called and the effect of vegetation on rockfall activity can be estimated. To eliminate the stochastic component of forest dynamics on rockfall activity, the same tree positions are repeatedly used during each rockfall simulation. Embedded in PICUS, the rockfall module is conceptually based on several core rules:

- (1) a boulder is defined as a sphere of variable size (diameter) and mass,
- (2) each rockfall trajectory starts either at a random or fixed location at the upper limit of the simulated forest stand,
- (3) the model distinguishes individual tree contacts (for trees higher than 1.3 m) and the energy dissipating effect of the regeneration layer, the so-called “understory”,

- (4) for the understory, vegetation is considered as distributed homogeneously over the patch in four height classes ($H_1 = 0\text{--}10 \text{ cm}$, $H_2 = 10\text{--}30 \text{ cm}$, $H_3 = 30\text{--}80 \text{ cm}$, $H_4 = 80\text{--}130 \text{ cm}$),
- (5) the boulder can change between rolling and jumping mode along its trajectory,
- (6) boulder trajectories are modelled in 3D space and
- (7) the trajectory ends when (i) the boulder leaves the simulated forest, or (ii) the boulder stops.

A moving boulder loses kinetic energy through (i) surface roughness (in rolling mode), (ii) movement through understory (in rolling or jumping mode), (iii) tree hits (in rolling or jumping mode), and (iv) through ground contact in jumping mode. Whether the boulder is jumping or rolling depends on a jumping criterion. A boulder starts jumping from the moment when the rotational velocity exceeds the translational velocity (compare Dorren et al., 2004).

Based on Meißl (1998), the acceleration of a rolling boulder without vegetation contact (a_g) is calculated as a function of current slope and surface roughness:

$$a_g = \frac{5}{7} g(\sin(\text{slope}) - \mu \cos(\text{slope})), \quad (4)$$

where a_g is the acceleration of a rolling boulder without vegetation contact [m s^{-2}], g the earth acceleration of gravity (constant 9.81 m s^{-2}), μ the parameter that defines surface roughness [0–1], and slope the inclination [$^\circ$].

If the boulder is jumping the path of the boulder is described by a ballistic parabola without consideration of air mass resistance. To account for the inclined slope the classical formulation was extended (Eqs. (5)–(7)). The height over ground ($h(t)$) of the boulder depends on the initial conditions of velocity (v_0), height (h_0) and the vertical dip angle relative to the horizontal (α_0) (compare Fig. 2a). Eq. (5) presents the jumping boulder without understory (“free jump”):

$$h(t) = -\frac{g}{2} t^2 + (\sin(\alpha_0) - \cos(\alpha_0)\tan(\text{slope}))v_0 t + h_0, \quad (5)$$

where $h(t)$ is the height over ground at time t [m], v_0 the velocity at $t = 0$ [m s^{-1}], α_0 the boulder dip angle at $t = 0$ [$^\circ$], h_0 the height over ground at $t = 0$ [m], slope the current slope in boulders direction [$^\circ$], and t the time [s].

As the time needed for reaching a specific height over ground (h_{above}) can be determined using Eq. (6), the jump distance can be calculated with Eq. (7):

$$t_h = \frac{1}{g} (v_0(\sin(\alpha_0) - \cos(\alpha_0)\tan(\text{slope})) + \sqrt{v_0^2(\sin(\alpha_0) - \cos(\alpha_0)\tan(\text{slope}))^2 + 2g(h_0 - h_{\text{above}})}), \quad (6)$$

$$d = v_0 t_h \cos(\alpha_0), \quad (7)$$

where t_h is the time needed for reaching h_{above} [s], h_0 the height over ground at $t = 0$ [m], h_{above} the height over ground [m], v_0 the velocity at $t = 0$ [m s^{-1}], α_0 the boulder

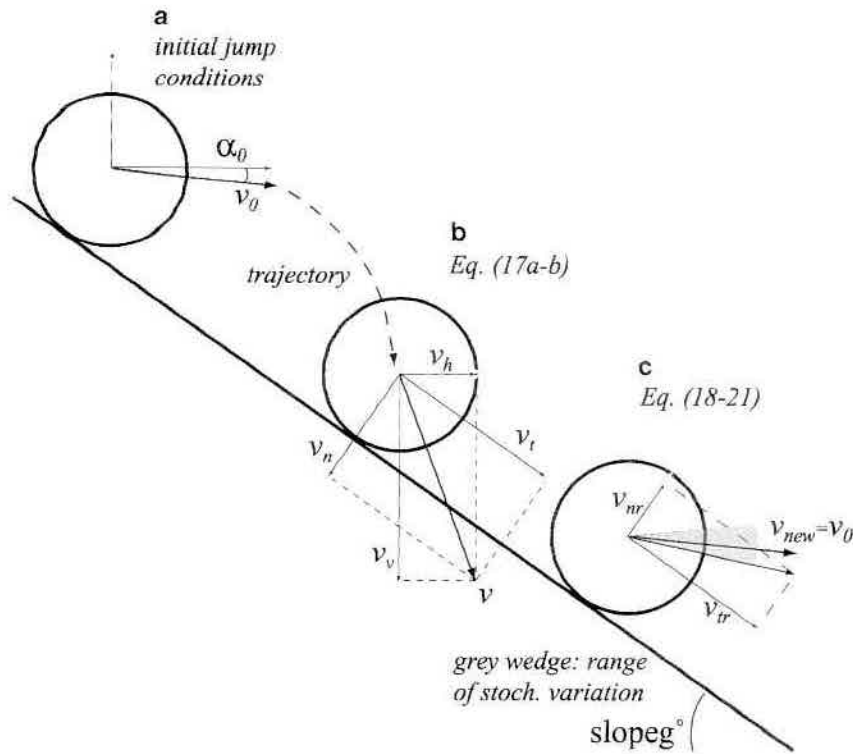


Fig. 2. Scheme for initial jump conditions (a) and ground contact (b, c). (a) Indicates the reference frame for boulder jumps (see Eqs. (4)–(7)). (b) shows the transformation of velocity components from the reference frame to the local slope coordinate system, and (c) the situation after the application of rebound parameters. The vector v_{new} describes the initial conditions for the next jump.

dip angle at $t = 0$ [°], and d the projected distance at time t [m].

2.2.2. Trajectory calculation through understory vegetation

In PICUS, trees that have a height lower than 1.3 m are not treated as individual trees but subsumed as understory. On each patch these small trees are grouped in four height classes: 0–10 cm, 10–30 cm, 30–80 cm, and 80–130 cm. The biomass within each height class is assumed as homogeneously distributed throughout the patch area (compare Section 2.1.1). In the rockfall module each of these height classes has a distinguishing energy dissipation value. For a given movement, distance d , biomass BM converted to its volume equivalent using specific density factors for small understory trees (Hochbichler, unpublished) V_{BM} and its attached fracture work U_{fr} (Berger et al., 2004) are accumulated within the corridor of the boulder, as defined by the boulder diameter. Currently, no empirical data on the fracture work of understory vegetation is available. As a preliminary solution the fracture work per unit volume U_{fr} has been derived from stress–strain diagrams of fresh wood (e.g., Berger et al., 2004).

For the boulder's rolling-mode, this distance-dependent energy loss is calculated as a constant negative acceleration a_s in Eq. (8a), in which F_s is the breaking force (Eq. 8(b)), and m the boulder mass. The resulting effective acceleration (Eq. (9)) in rolling mode is the sum

of Eqs. (4) and (8a):

$$a_s = \frac{F_s}{m}, \quad (8a)$$

$$F_s = -V_{\text{BM}} U_{\text{fr}} B, \quad (8b)$$

$$a_{\text{eff}} = a_g + a_s, \quad (9)$$

where a_s is the constant negative acceleration due to vegetation contact [m s^{-2}], F_s the constant breaking force [kg m s^{-2}], m the boulder mass [kg], V_{BM} the volume equivalent of dry mass of understory [$\text{m}^3 \text{m}^{-2}$], U_{fr} the fracture work [J m^{-3}], B the boulder diameter [m], a_g the velocity of a rolling boulder without vegetation contact [m s^{-2}], and a_{eff} the effective acceleration (including vegetation contact) [m s^{-2}].

Movement through the understory in the jumping mode is solved iteratively. For each iteration step (step length 0.2 m) the jump height-specific biomass density is retrieved from the understory height classes and the derived deceleration is calculated, resulting in reduced movement velocity and jump length, where the decelerating effect of the understory is inversely proportional to boulder diameter.

2.2.3. Effect of tree hits and ground contact on boulder trajectory

2.2.3.1. Tree hits. Energy loss due to boulder-tree collision is calculated in the same manner for the jumping and

the rolling mode. As long as neither trees nor ground surface are hit, the boulder trajectory direction stays constant. Therefore, it is possible to identify the next tree hit deterministically. While this calculation is carried out in a vector approach, the eccentricity of the boulder-stem impact is stochastically determined within the range set by the tree diameter under bark, accounting also for the not perfect spherical form of boulders under real world conditions. Assuming only limited elastic reaction of the stem during impact, the new deviation angle can be calculated based on eccentricity of the contact point relative to the stem axis and the tree's DBH.

Depending on the eccentricity of the collision, part of the boulder's energy is directed to the centre of the tree. The kinetic energy of a boulder immediately before a tree contact is fractioned by splitting the velocity vector v_0 into its radial (v_r) and tangential (v_t) component, respectively (Eqs. 10(a) and (b)). As a prerequisite the angle between the boulder's direction and the tree centre is calculated with Eq. (11) (see Fig. 3):

$$v_r = v_0 \cos(\delta), \quad (10a)$$

$$v_t = v_0 \sin(\delta), \quad (10b)$$

$$\delta = \arcsin\left(\frac{e}{\text{DBH}0.5}\right), \quad (11)$$

$$W_r = \frac{m}{2} v_r^2, \quad (12)$$

where e is the randomly selected impact position related to tree diameter under bark [cm], δ the angle between boulder direction and tree centre [°], v_0 the velocity of boulder before impact [m s^{-1}], v_r the component of velocity in radial direction [m s^{-1}], v_t the component of velocity in tangential direction [m s^{-1}], and W_r the kinetic energy in radial direction [J].

The radial component of the kinetic energy W_r (Eq. (12)) is compared to the energy dissipation potential of the tree (Eq. (13)). Tree volume is calculated according to Pollanschütz (1974). After the radial energy component

W_r is reduced up to that limit (Eq. (14)), the remaining velocity after the impact is calculated with Eqs. 15(a) and (b). Friction loss of v_t is currently not considered:

$$W_{\text{tree}} = V_{\text{tree}} U_{\text{fr}}, \quad (13)$$

$$W_{r\text{-out}} = \max(0; W_r - W_{\text{tree}}), \quad (14)$$

$$v_{r\text{-out}} = \sqrt{\frac{2W_{r\text{-out}}}{m}}, \quad (15a)$$

$$v_{\text{out}} = \sqrt{v_t^2 + v_{r\text{-out}}^2}, \quad (15b)$$

where W_{tree} is the energy dissipation potential of the tree [J], V_{tree} the tree stem volume [m^3], U_{fr} the fracture energy per m^3 wood [default: 90000 J m^{-3} (Berger et al., 2004)], $W_{r\text{-out}}$ the kinetic energy in radial direction after impact [J], $v_{r\text{-out}}$ the velocity in radial direction after impact [m s^{-1}], and v_{out} the velocity of boulder after impact [m s^{-1}].

If the energy dissipation potential of the tree is exceeded by W_r , the stem breaks and the outgoing horizontal deviation angle is reduced according to Eq. (16a) (compare Fig. 3). The final deviation angle 'dev' is calculated with Eq. (16b):

$$\text{dev}_{\text{mod}} = \arctan\left(\frac{v_{r\text{-out}}}{v_t}\right), \quad (16a)$$

$$\text{dev} = \begin{cases} \delta < 0 : -90 - \delta + \text{dev}_{\text{mod}}, \\ \delta \geq 0 : 90 - \delta - \text{dev}_{\text{mod}}, \end{cases} \quad (16b)$$

where dev_{mod} is the reduction of horizontal deviation due to stem breakage [°], and 'dev' the resulting deviation after tree hit [°].

2.2.3.2. Ground contact. Energy dissipation by ground contact after jumping is calculated based on empirical rebound factors (Chau et al., 2002; Azzoni et al., 1995; Pfeiffer et al., 1993) that reduce boulder velocity (Eqs. (17) and (18)). The rebound factors comprise of a normal (reboundN) and a tangential (reboundT) component relative to ground surface, where an impact without energy loss (e.g., a rubber ball on concrete) has a value of 1 and a total reduction of the boulder energy has a value of 0. The new boulder velocity v_{new} is then calculated with Eq. (19). The outgoing angle relative to the slope dip angle (Eq. (20)) is adjusted by a stochastic component to account for deviating effects of micro-topography, e.g. rocks or dead wood. Following Pfeiffer et al. (1993) the maximum adjustment is set by a roughness parameter for deviation, here 20° (Eq. 21). Figs. 2(b) and (c) give a schematic representation of these geometrical components. The natural tendency of a boulder to approach the slope direction is taken into account through bisection of the outgoing horizontal trajectory direction deviation angle plus a randomly chosen angle. Based on empirical findings by Berger et al. (2004) this horizontal deviation after surface contact is evenly distributed and varies between

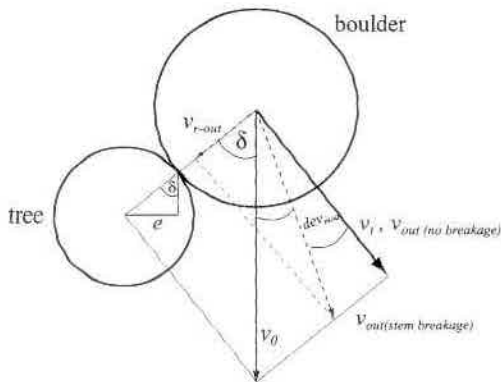


Fig. 3. Geometric scheme of the boulder-tree impact. If the tree does not break, the resulting $v_{r\text{-out}}$ is zero. In that case the outgoing velocity vector is v_t . Otherwise the outgoing velocity is the sum of v_t and $v_{r\text{-out}}$.

+20° and −20°. In the current model version boulders that leave the simulated area on the sides are not tracked any further.

$$v_n = v_v \cos(-\text{slopeg}) - v_h \sin(-\text{slopeg}), \quad (17a)$$

$$v_t = v_v \sin(-\text{slopeg}) + v_h \cos(-\text{slopeg}), \quad (17b)$$

$$v_{nr} = v_n \text{ reboundN}(-1), \quad v_{tr} = v_t \text{ reboundT}, \quad (18a-b)$$

$$v_{\text{new}} = \sqrt{v_{nr}^2 + v_{tr}^2} \quad (19)$$

$$\theta = \arctan\left(\frac{v_{nr}}{v_{tr}}\right), \quad (20)$$

$$\alpha_0 = -\text{slopeg} + \theta + \text{nrandom}(0, \text{rough}), \quad (21)$$

where *slopeg* is the slope in current boulder's direction [°], v_n the boulder velocity normal to slope [m s^{-1}], v_t the boulder velocity tangential to slope [m s^{-1}], v_v the vertical boulder velocity [m s^{-1}], v_h the horizontal boulder velocity [m s^{-1}], v_{nr} the v_n reduced with rebound parameter [m s^{-1}], v_{tr} the v_t reduced with rebound parameter [m s^{-1}], v_{new} the new boulder velocity after ground contact [m s^{-1}], θ the outgoing boulder angle relative to *slopeg* [°], α_0 the adjusted outgoing boulder angle relative to horizontal plane [°], *reboundN* the rebound parameter normal to slope [0–1], *reboundT* the rebound parameter tangential to slope [0–1], and *rough* the maximum outgoing jump angle (here: 20°).

2.3. Model evaluation experiments

2.3.1. Experiment 1: Sensitivity analyses

Sensitive model parameters can guide applications and model improvement (Vanclay and Skovsgaard, 1997). Furthermore, awareness of parameter sensitivity can add interpretive value to the evaluation results and highly sensitive parameters can be varied in the evaluation experiments in order to explore their influence on the simulation results. In the current study the sensitivity of the rockfall module output to parameters which are either crucial to determine or of obvious relevance to rockfall processes is evaluated in a comprehensive sensitivity analysis (Table 1). The effect of a 10% change of a single parameter on the target value “mean run out distance” (ROD_m) over the simulated area will be compared to a base scenario. This scenario consists of a forest stand with a ground surface of 300 m downslope times 100 m in width on which 400 trees ha^{-1} (*Picea abies*), each with a DBH of 40 cm, are randomly placed. The simplified stand characteristics for this experiment are chosen based on former work of Wasser and Frehner (1996). ROD_m is calculated over 1000 boulder trajectories, repeated 50 times on the same tree pattern ($n = 50$). Boulders leaving the simulated forest at the sides are not taken into account. The tree positions are fixed and kept for all runs.

Table 1

Parameters of the rockfall module and their base value for the sensitivity analyses

Parameter	Base value	Unit
Slope	30	[°]
ReboundN	0.7	Dimensionless
ReboundT	0.8	Dimensionless
Rough	20	[°]
μ	0.5	Dimensionless
Boulder size	50	[cm]
Stem density	400	stems ha^{-1}
DBH	40	[cm]
Enter velocity (1)	0.8	[m s^{-1}]
Enter velocity (2)	10.0	[m s^{-1}]

Slope = hillslope, ReboundN = restitution coefficient normal to the slope (dampening effect), ReboundT = restitution coefficient tangential to the slope (dampening effect), Rough = range of stochastic variation of the outgoing vertical angle after ground contact, μ = surface roughness for rolling mode, boulder size = boulder diameter, DBH = tree diameter at 1.3 m height, enter velocity = initial boulder velocity.

Table 2

Stand initialization characteristics for model inter-comparison Experiments 2 and 3

Species	DBH-class [cm]	Age [years]	Trees [n ha^{-1}]	H/D
<i>Picea abies</i>	8–9	40	600	85
<i>Picea abies</i>	9–10	40	600	75
<i>Picea abies</i>	10–11	40	600	70

H = mean tree height [cm], D = mean tree diameter [cm].

2.3.2. Experiments 2 and 3: Model intercomparison

In order to compare the rockfall module with existing modelling approaches, the development of two key output variables of the new tool is compared in a 100 year simulation with recent formulations from the literature. For both experiments the initial stand is a pole stage stand (Table 2) which develops over the 100-year simulation period without active management intervention. The regeneration module is deactivated. Climate and soil conditions represent a site in the Eastern Alps at an altitude of 1450 m a.s.l.

First, in Experiment 2, a key parameter to evaluate rockfall protection efficiency, the Average Distance between Contacts (ADC), as simulated with 1000 rockfall trajectories in the rockfall module, is compared with the ADC following Gsteiger (1993). Thereby the calculation formula of Gsteiger (1993) is applied to the simulation output according to Eq. (22). The ADC in the rockfall module is calculated as the mean trajectory length, divided by the average number of tree hits over 1000 simulated trajectories. The simulated stand extends 300 m downslope and has a width of 100 m:

$$\text{ADC}_{\text{Gsteiger}} = \frac{A}{[(N B) + \sum \text{DBH}]}, \quad (22)$$

where A is the simulated area [m^2 , horizontal area], N the stem number [on simulated area], B the boulder size [m], and DBH the diameter at breast height [m].

Next, in Experiment 3, the energy dissipation (Edisp) by trees along the boulder's trajectory, calculated as a mean over 1000 trajectories in the rockfall module, is compared to the calculation method of Brauner et al. (2005). In their approach, Edisp by trees is calculated as the dissipation potential of n average trees that are fully hit along a complete trajectory through the simulated stand (Dpath) (compare Eq. (23)). The dissipation potential of an average tree represents the maximum boulder impact the tree can withstand without breaking. The number of tree hits along the trajectory is calculated by dividing the horizontal trajectory length (Dpath) with the expected distance between tree hits assuming a regular tree pattern. According to Brauner et al. (2005) this distance represents a boulder's travelling distance within which a tree impact occurs with a probability of 90%. For details we refer to Brauner et al. (2005). Stand data for the calculations were taken from the PICUS simulator.

In the PICUS rockfall module the dissipated energy by the trees is summed individually over the energy radially directed to the tree centre, as calculated in Section 2.2.3.1. The simulated stand extends over $100 \text{ m} \times 100 \text{ m}$:

$$\text{Edisp}_{\text{Potential}} = \frac{\text{Dpath}}{\text{D90}} (V_{\text{tree}} U_{\text{fr}}), \quad (23)$$

where Dpath is the horizontal trajectory length of the boulder [m], D90 the boulder travelling distance till first hit with passing probability 0.9 [m], V_{tree} the volume of average tree [m^3], and U_{fr} the fracture work [J m^{-3}].

2.3.3. Experiment 4: Sensitivity to forest management

To evaluate how sensitive the new modelling approach responds to realistic forest management, three stands under three different management regimes each are evaluated for their rockfall protection function. Each scenario run extends over a simulation period of 100 years. The target variable is ROD_m . The study stands are located in Tyrol, central Alps in Austria. Notwithstanding the broad diameter distributions (compare Fig. 4) all stands are mono layered. In none of the stands active management interventions have been implemented over the last 20 years. Stand data and observations were provided by the NAB-project "Natural Potential of Alpine Regions". Representative soil data was taken from the Austrian Forest Soil Survey (Englisch et al., 1991), monthly climate data were interpolated from nearby weather stations. Table 3 gives major stand characteristics. In all stands regeneration is lacking, in stands A and B mainly due to low light levels at the forest floor. In stand C, several large gaps occur with gap diameter as large as 30 m. Local forest managers report severe browsing impact of cattle and ungulates. *Picea abies* is the dominant species in all stands.

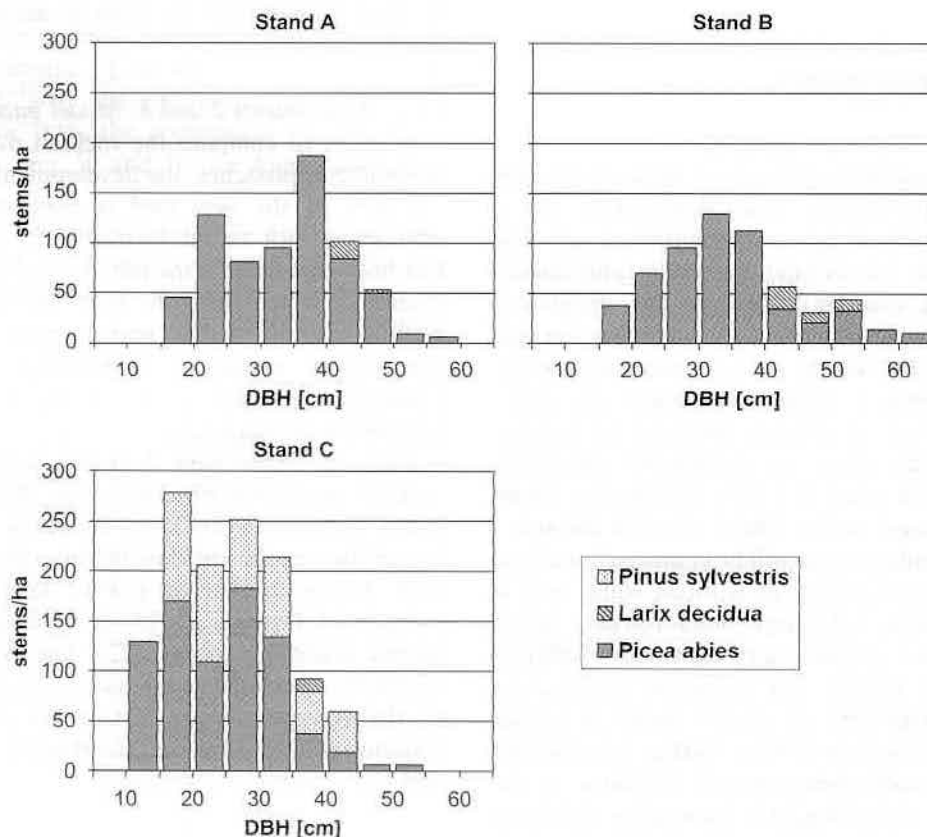


Fig. 4. Initial DBH distribution for stands A, B and C (Anonymous, 2005).

Table 3
Stand characteristics for stands A, B and C.

Stand characteristics	Stand A				Stand B			Stand C			
	PA	PS	LD	Total	PA	LD	Total	PA	PS	LD	Total
Slope [°]	—	—	—	27	—	—	35	—	—	—	39
Age [years]	170	125	195	—	175	158	—	194	158	145	—
Mean height [m]	25.8	25.0	27.0	—	30.0	33.3	—	21.3	15.7	19.0	—
MAI ₁₅₀ [m ³ ha ⁻¹]	4.9	—	—	—	6.2	—	—	2.6	—	—	—
Basal area [m ² ha ⁻¹]	64.0	1.0	3.0	68.0	58.0	10.0	68.0	41.3	26.7	1.3	69.3
Stem number per ha	689	5	20	714	558	61	619	801	434	12	1247
Stocking density	1.26	0.02	0.10	1.38	1.11	0.24	1.35	0.88	0.55	0.04	1.47
Volume [m ³ ha ⁻¹]	722	11	34	767	762	135	897	386	207	11	604

PA = *Picea abies*, PS = *Pinus sylvestris*, LD = *Larix decidua*, MAI₁₅₀ = mean annual increment at stand age 150, stocking density = stand basal area relative to basal area of yield tables (Anonymous, 2005).

The stand data had been sampled spatially non-explicit. For stand C a qualitative description of gap distribution was available. In the simulation, in stands A and B trees are randomly distributed over all patches, whereas in stand C no trees were assigned to patches that represent gaps. The initially assigned position of the trees was kept for all simulation runs. For all simulations the patch array consists of 10 × 30 patches (3.0 ha).

To analyse the response of the new rockfall module to stand structures as affected by management three-stand treatment programmes (STP) are applied to each stand over a simulation period of 100 years, starting in year 2005. STP1 is a “no intervention” regime, STP2 is a “business as usual” regime, and STP3 represents a “rockfall protection management” regime (compare Tables 4a and b). The passive “no intervention” regime is used here as a natural benchmark scenario with which the protective effect of the active management regimes can be compared. STP2 is a regime commonly applied to regenerate mature mountain forests managed for timber production. First, a regeneration cut opens up the stand to initialize regeneration, and later a final cut removes the shelter. In the simulation trees with a DBH smaller than 12 cm are retained. During the early stem exclusion phase (*sensu* Oliver and Larson, 1996) a pre-commercial thinning is applied. In STP3 the stands are managed according to Wasser and Frehner (1996) with a focus on stand stability. In general, the mature single layered, homogeneous stands are to be transformed into stands with at least groups of trees of different ages and size classes. Such a transformation towards enhanced stability is best accomplished with slight interventions (Ott et al., 1997). STP3, therefore, includes several thinning with intervals of 20 years. Furthermore, gaps are created and successively enlarged in stands A and B to enhance natural regeneration. Treatment of stand C differs from stands A and B with regard to several features. As productivity in stand C is considerably lower, the shelter period of STP2 extends over 35 years compared to 20 years for stands A and B. The eight initial gaps in 2005 are already 4–12

Table 4(a)
Stand Treatment Programmes (STP2 = business as usual management, STP3 = protection forest management) for stands A and B

Simulation year	STP2		STP3		
	Type	Removal [%]	Type	Removal [%]	Gaps × patches
2010	Regeneration cut	40	Thinning/gap	25/10	4 × 8
2030	Clearing	100	Thinning	25/10	—
2050	—	—	Thinning/gap	25/10	4 × 16
2070	—	—	Thinning	25/10	—
2075	Pre-thinning	50	—	—	—
2090	—	—	Thinning/gap	25/10	4 × 24

The intensity for thinnings in STP3 distinguishes a removal percentage (related to stem numbers) for the stability thinning (DBH: 12–41 cm), respectively the overhead thinning (DBH > 41 cm). The 4 gaps created in 2010 (STP3), each 8 patches in size, are enlarged every 40 years with another 8 patches. Start of the simulation in year 2005. Simulated area: 3.0 ha.

Table 4(b)
Stand Treatment Programmes (STP2 = business as usual management, STP3 = protection forest management) for stand C

Simulation year	STP2		STP3	
	Type	Removal [%]	Type	Removal [%]
2010	Regeneration cut	40	Thinning	20/10
2030	—	—	Thinning	20/10
2045	Clearing	100	—	—
2050	—	—	Thinning	20/10
2070	—	—	Thinning	20/10
2075	—	—	—	—
2090	Pre-thinning	50	Thinning	20/10

The intensity for thinnings in STP3 distinguishes a removal percentage (related to stem number) for the stability thinning (DBH: 12–41 cm), respectively the overhead thinning (DBH > 41 cm). Start of the simulation in year 2005. Simulated area: 3.0 ha.

patches in size and not enlarged in STP3. Tables 4a and b give a complete list of silvicultural interventions (see Appendix A).

3. Results

3.1. Parameter sensitivity and model comparison

In Experiment 1, the influence of the parameters initial velocity of the boulders and *rough*, the range of variation of the vertical outgoing angle after ground contact, on the mean run out distance (ROD_m), calculated over 1000 simulated trajectories, is indifferent according to Fig. 5. With an initial velocity of 0.8 m s^{-1} ROD_m is 118 m, a 10% increase in v_{init} results in an increase in ROD_m by 0.8%, while a 10% decrease reduces ROD_m by 1.4%. The same experiment with an initial base velocity of 10 m s^{-1} yields a mean runout distance of 229 m, and a sensitivity of +0.9% and -3.0%, respectively. In a Kolmogoroff-Smirnoff-Test for independent samples, for both initial base velocities the ROD_m distributions for $\pm 10\%$ initial velocity proved to be not significantly different ($\alpha = 0.05$) from the distribution of the base scenario. Without a regeneration layer the parameter ROD_m is highly sensitive to *slope* and μ (surface roughness in rolling mode) which meets expectations. ROD_m is intermediate sensitive to the other tested parameters with relative sensitivity of ROD_m between

10% and 20% compared to the baseline. The stem number per ha is more influential than the mean tree diameter.

Fig. 6 shows the comparison of the ADC according to Gsteiger (1989) and the corresponding parameter as calculated from the output of the PICUS rockfall module (Experiment 2). The two parameters are highly correlated ($r_p = 0.998^{**}$) but the ADC after Gsteiger is moderately larger. As shown in Fig. 7 the dissipated energy ($Edisp_{Betal}$) as estimated with the approach of Brauner et al. (2005) has an increasingly higher value compared to the values from the PICUS rockfall module ($Edisp_{PRM}$) (Experiment 3). Obviously, $Edisp_{Betal}$ is closely related to increasing stand volume (V), while $Edisp_{PRM}$ is not. Initially, the two estimates have similar values. As stem number decreases, the difference in the number of tree hits between the two approaches first approaches zero, then the number of tree hits in PICUS is slightly lower compared to the calculation according to Brauner et al. (2005).

3.2. Sensitivity to forest management

The effects of the stand treatment programs on the rockfall protection function in Experiment 4 were char-

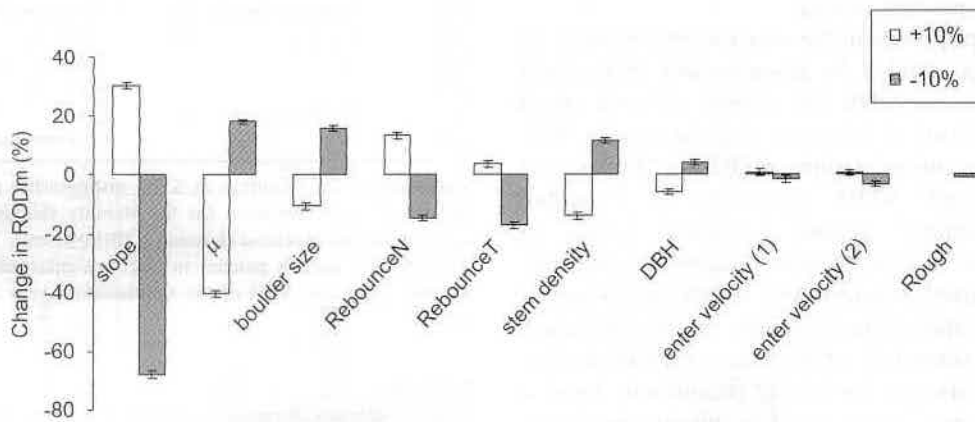


Fig. 5. Percentage change in mean run out distance (ROD_m ; based on 1000 boulders) of 50 cm diameter boulders as a result of either 10% increase or decrease of the selected parameters (compare Table 1). The confidence intervals are calculated with $\alpha = 0.05$. (Experiment 1). ($n = 50$).

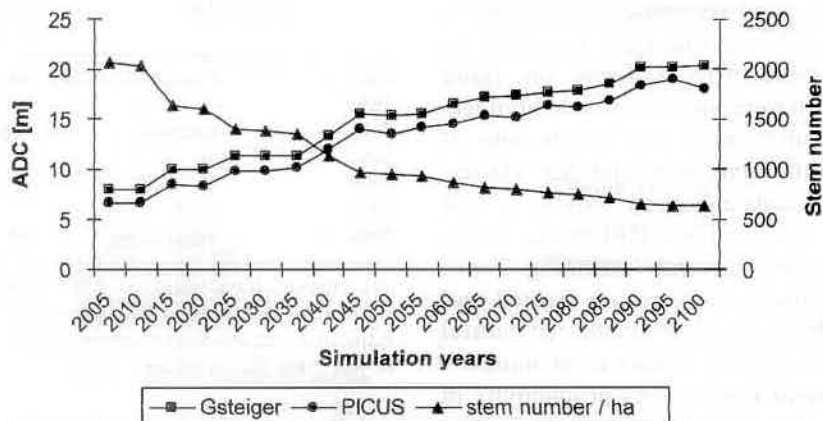


Fig. 6. Average Distance between Contacts (ADC) calculated with two approaches for 50 cm boulder diameter (1000 repetitions) over 100 years of forest development (Experiment 2).

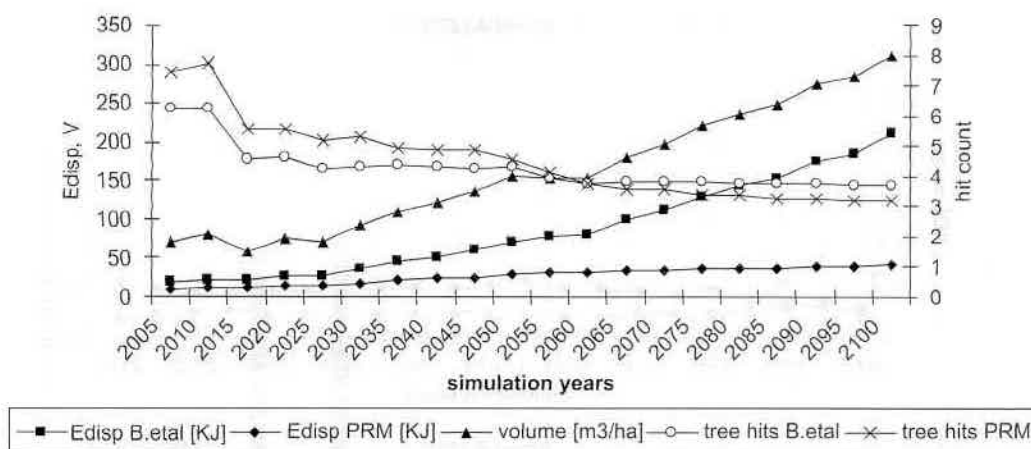


Fig. 7. Kinetic boulder energy [kJ] dissipated by tree hits along the trajectory, calculated as a potential (Edisp B.etal) based on Brauner et al. (2005), and simulated with the rockfall module of PICUS (Edisp PRM). The number of tree hits over which Edisp is calculated is shown on the secondary y-axes. (Experiment 3).

acterized by the mean run out distance (ROD_m). When comparing the ROD_m between the stands, the run out distances in stand A are considerably shorter than in the other stands mainly due to the steeper slope in stands B and C (compare Table 3). When comparing the effect of the management regimes between the stands, there are similar patterns for all STPs in stands A and B, but different effects for STP1 (“no intervention”) and STP3 (“protection forest management”) in stand C (compare Fig. 8).

In all stands the “business as usual” management regime STP2 causes the largest variability in ROD_m over time. At first, when regeneration is missing and the canopy is opened, the mean run out distances under STP2 more than double. Then, when natural regeneration emerges in considerable densities as simulated with the regeneration module, ROD_m decreases strongly. Only when tree density decreases after the pre-commercial thinning, ROD_m increases again. At least for stands A and B, STP1 gives stable run out distances and even decreasing distances later on when natural regeneration emerges due to a reduction of stem numbers through natural tree mortality. However, in stands A and B over most of the simulation period ROD_m under STP1 is substantially higher than under any of the other treatments.

Contrary to the “no intervention” strategy (STP1), the “protection regime” (STP3) allows for more natural regeneration due to the actively initialized gaps and the regular thinnings. STP3 first causes an increase in ROD_m after the first interventions, but soon results in stable and lower values of ROD_m . The mean run out distance is then shorter than under STP1.

More complicated is the analyses for stand C, in which under STP2 and in the “no intervention” strategy (STP1) the initial gaps in the simulation are soon filled with regeneration, and therefore, no significant difference in ROD_m for STP1 and STP3 can be found until simulation year 2085 (compare Fig. 8). From 2085 on STP3 shows

clearly lower ROD_m than STP1. Due to rapid and abundant regeneration after the first shelterwood cut ROD_m under STP2 drops to very low values, which then slowly increase again due to reduced stand density. Under the assumption that no regeneration would emerge in stand C, STP1 has a constant shorter ROD_m than STP3, caused by the thinnings in the latter treatment which reduce stem numbers faster than natural mortality in STP1 without substantially affecting ROD_m via enhanced individual tree growth. Consequently, STP2 with a 40% reduction in stem numbers in year 2010 without any regeneration establishment provides the least protection against rockfall.

While ROD_m is not giving much information on the probability that a boulder can reach a specific distance within the simulated stand, as an example the result of STP3 in stand B is also presented in run out distance classes (Fig. 9). It can be seen that, for instance, in 2005 approximately 60% of the boulders were stopped within the first 100 m after entering the simulated forest stand. This figure increased to 68% of the boulders being stopped after 200 m trajectory length.

4. Discussion and conclusions

Through integration of the newly developed 3D rockfall module in the forest simulator PICUS, including an extended regeneration module, a new research tool has been developed. It bears the potential of assessing the development of the protective effect of a forest ecosystem against rockfall events over longer time periods in managed and unmanaged forests. Thereby, it answers to the call for a tool that takes explicitly into account both, rockfall and forest development. PICUS operates at the spatial scale of 100 m² patches where the position of the trees within a patch is not known. This approach allows the application of simplified competition and light models in simulating forest dynamics, while on the other hand it lacks information required for the spatially explicit simulation

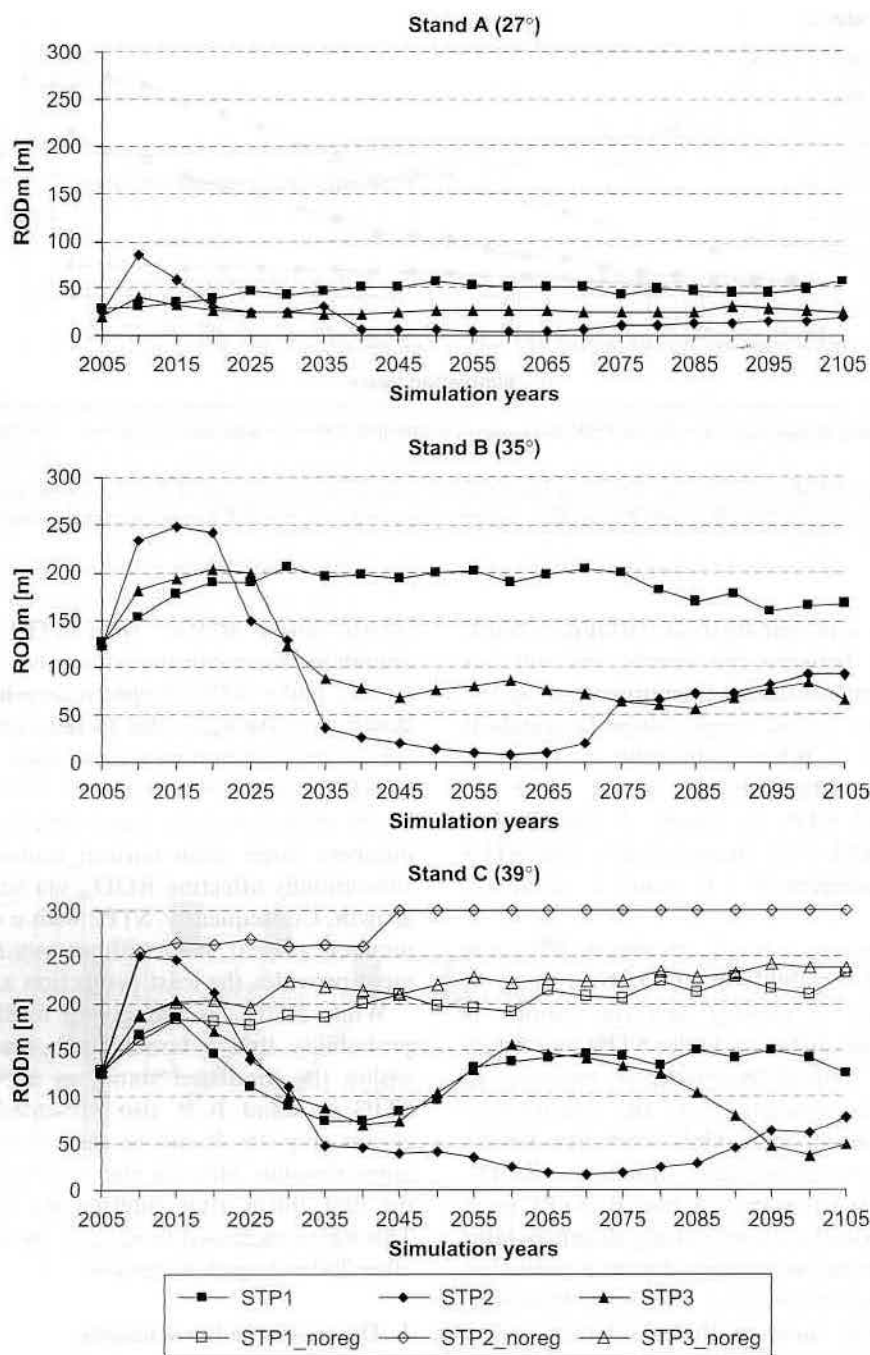


Fig. 8. Effect of forest management on the mean run out distance (ROD_m) for stands A, B and C over a period of 100 years. Boulder size is 50 cm. STP1 = “no intervention” regime, STP2 = “business as usual” regime, STP3 = “protection forest management” regime. For stand C the simulations are also presented for a situation where regeneration is lacking (noreg). (Experiment 4).

of rockfall activity. To bridge this gap, in the presented approach the trees within a patch are either assigned random positions or measured tree coordinates are provided which are then exclusively utilized by the rockfall module while forest dynamics are still simulated at $100m^2$ -resolution. The approach allows the 3D simulation of single boulder trajectories, which in turn makes stochastic components in the rockfall module inevitable. This stochasticity makes an individual boulder trajectory a chance event and an appropriate number of repetitions are

needed in order to evaluate rockfall and protection effect. The variability of simulated indicators for rockfall activity depends on the interplay of site, stand and boulder characteristics and may differ among applications. The relationship of an increase in rockfall process indicator variability with decreasing stand density can be used as a general guideline. A detailed analysis was beyond the scope of this contribution which focused on model development and preliminary model evaluation experiments, and will be covered elsewhere.

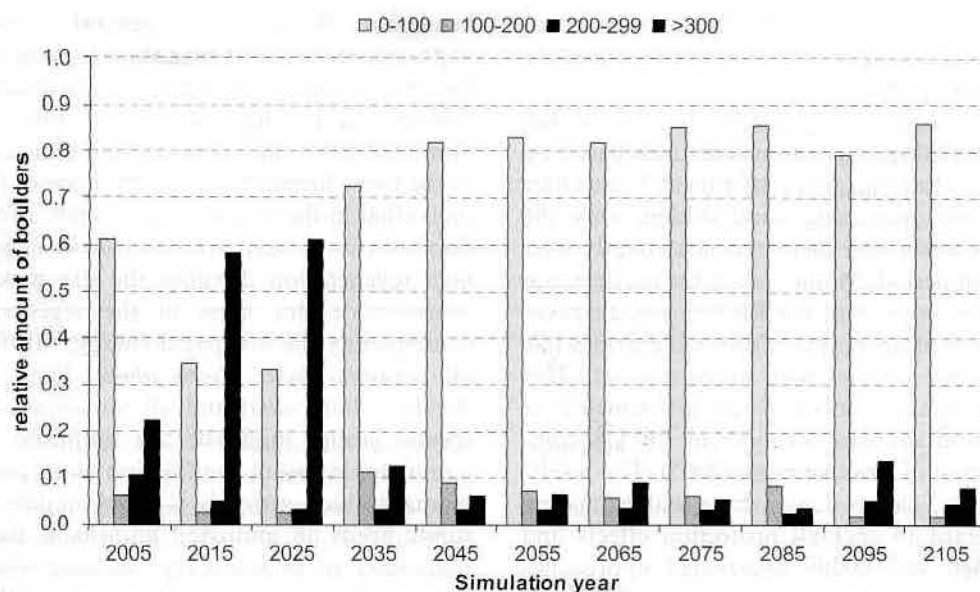


Fig. 9. Relative distribution of run out distances in stand B represented in run out distance classes [m], for a simulation period of 100 years under protection forest management (STP3) in Experiment 4.

In the new rockfall module, most of the processes that describe a rockfall trajectory through a forest stand are incorporated. These processes are modelled as a mix of physics and empirical formulations as expressed by “black box” parameters. The empirical algorithms concern mainly the events where boulder energy is absorbed by ground contact. These algorithms are parameterised from findings of empirical studies (e.g., Berger et al., 2004). Processes that are not yet taken into account are the explicit consideration of dead wood on the forest floor (Schönenberger et al., 2005), and snags including stumps with decreasing potential to dissipate energy due to decay processes. Another feature particularly relevant in longterm simulations of rockfall protection forests is reduced tree vitality due to damage from hits by rocks which very likely affect tree mortality (compare Vospernik, 2002) as well as energy dissipation potentials.

That refining the empirical components may be an efficient approach to improve the reliability of the rockfall module is further supported by the results of the sensitivity analysis in Experiment 1 where, for instance, the empirical rebound parameters showed substantial impact on simulated run out distances. In the presented experiment the effects of selected key stand attributes on ROD_m are of similar magnitude with stem numbers being slightly more influential than mean tree diameter Dorren et al. (2005) report that the influence of stand density and mean tree diameter on the protection effect varies over the range of boulder sizes with mean tree diameter being more important for larger rocks. The fairly small differences in ROD_m sensitivity for stand density and mean tree diameter respectively indicates that the tested boulder size of 50 cm may just be of that intermediate size beyond which stand

density becomes less influential compared to mean diameter.

In relative terms both levels of initial boulder velocities tested in Experiment 1 just slightly affect simulated ROD_m . Thus, given the difficulties in estimating initial boulder velocity for a specific model application in transit zones robust model results can be generated. However, care has to be taken in extrapolating the results of the sensitivity experiment to other conditions due to the complex interplay of site, stand and boulder characteristics.

To better understand the behaviour of the new rockfall module it was compared to two approaches from the literature which do not simulate explicitly rockfall trajectories but instead apply simplifying static assumptions. First, the widely used ADC concept indicating the average distance between boulder-tree contacts calculated after Gsteiger (1989) was compared with equivalent simulation output of the rockfall module. Results of the two approaches correlated closely. However, ADC after Gsteiger was consistently 1–3 m larger than the corresponding figure from the PICUS simulation. Notwithstanding that the divergence in the average distance among tree hits among the two approaches were quite small, to better understand the conceptual differences among the approaches several contrasting issues need to be considered. Taking samples for distances between trees over a randomly distributed tree pattern, gives Poisson-like distributions which lowers the mean value over all samples, relative to a regular tree pattern (Stoyan and Stoyan, 1992) which is one of the assumptions in the ADC approach by Gsteiger (1989). A further explanation for shorter ROD_m in the PICUS module is that most boulders in the simulation stop before reaching the maximum distance of 300 m which makes the trajectory relative to the amount of

tree hits shorter, and thereby also the ADC. In contrast, with the less realistic formula of Gsteiger the trajectory deterministically ends at 300 m.

In comparing the energy dissipated by the trees within the rockfall module ($\text{Edisp}_{\text{PRM}}$) and calculations based on Brauner et al. (2005) ($\text{Edisp}_{\text{Betal}}$) in Experiment 3, the latter increased steadily with increasing stand volume while the former was always lower and increased just slightly over the entire simulation period. Major reason for the deviance between the approaches is, that the PICUS module takes realistically into account only radially directed energy while $\text{Edisp}_{\text{Betal}}$ assumes full contact with every tree hit. This effect is intensified by the number of tree hits which over the simulation period decrease stronger in PICUS compared to the algorithm of Brauner et al. (2005). The results of Experiments 2 and 3 clearly demonstrate that estimating potentials with regard to rockfall protection effects and employing simplified and highly aggregated approaches might strongly overestimate the protection effect of forests, and that explicit rockfall simulation clearly bears the potential to provide more reliable results.

Before discussing the results of Experiment 4 the issue of integrating understory in the new rockfall module will be addressed. In recent years several rockfall models have been presented (e.g., Dorren et al., 2004; Perret et al., 2004; Brauner et al., 2005). However, most if not all entirely focus on the effect of adult trees on rockfall activity. Nevertheless, understory may play an important part in reducing runout distances of boulders as well as in preventing the start of boulder trajectories. In the current study we attempted to extend the rockfall simulation by explicitly considering understory vegetation. The original approach to model tree regeneration in PICUS was a recruitment model (compare Vanclay, 1994), initializing new saplings at breast height (1.3 m). The new regeneration model in PICUS is a size class model and simulates the development of regeneration through four height classes from establishment of seedlings until the saplings enter the model as individual trees. For this contribution a generalized parameterization based on qualitative information from the literature was used. Simulation experiments aiming at regeneration composition and density along ecological gradients yielded promising results when compared to qualitative data (e.g. Müller, 2003; Ruhm, 2004).

While in general the processes mimicking boulder movement and hits with trees larger 1.3 m height are fairly well established, the effect of the understory on rockfall processes as currently implemented in PICUS has to be seen as a set of hypotheses. Due to the novelty of this approach it was impossible to provide empirical data for the effect of understory on rockfall processes, neither for model development nor for model validation. Clearly, this identifies a knowledge gap and calls for targeted research. Analysis of simulated ROD_m when shifting from a stand development phase consisting exclusively of saplings in height class H4 (80–130 cm) to a stand structure with trees just grown out of H4 showed a reasonably smooth

behaviour. While this in general supports the current approach, there are at least three aspects showing potential for improvement: (i) while in the regeneration module competition for light within the four height classes is estimated from cumulated sapling biomass at least as high as the focus height class, the dry mass of the representative individual in the height classes is not affected by competition but can be seen as a broad-scale mean value. Thus, at high regeneration densities the dry mass allometry may overestimate dry mass in the regeneration layer and consequently the dissipated energy; (ii) the aggregation of all conifers (here: *Picea abies*, *Pinus sylvestris*, *Larix decidua*, *Abies alba*) and all broadleaves into two broad species groups might be too simplistic. (iii) Finally, the parameterisation of the fraction work per unit understory biomass which currently is based on data from larger trees surely needs an improved knowledge base. These limitations have to be taken into account when discussing the results of Experiment 4 which addressed the response of the rockfall module to stand management interventions.

The alternative management scenarios, applied to three different mountain forest stands (Experiment 4) indicated that the rockfall module is sensitive to management interventions, and that the relative magnitude of the response appeared realistic. Furthermore, the runs showed the potential of the module to evaluate the protective effect of alternative management interventions and to compare them with the protective effect of stand development without active management. The latter may save cost, but fail in providing protection in a sustainable way. It has to be noted that so far no integrated simulation tool able to realistically mimic heterogeneous silvicultural management and stand structures had been available. Although the protective effect of the regeneration layer may have been overestimated by the current model version, the results indicated the importance of successful regeneration establishment and development in mountain forests. It is important to note that Experiment 4 was not intended to evaluate specific protection forest management concepts but was exclusively aimed at analysing the sensitivity of rockfall activity to realistic silvicultural interventions. Prior to evaluating proposed management concepts for protection forests the knowledge gaps regarding, for instance, the protective effect of understory have to be addressed. To indicate the effect of unsuccessful silvicultural regeneration measures the management scenarios for stand C were simulated twice: one time with abundant and continuous regeneration establishment, a second time without any regeneration success at all. This clearly indicates the potential negative impact of intensive browsing by ungulates and cattle in sustainable mountain forest management and renders the inclusion of browsing as a model feature in specific assessments of silvicultural concepts for mountain forest management a necessity (e.g., Eiberle, 1989).

To further underpin the realism and accuracy of the new rockfall module in simulating rockfall trajectories on

Table A1
Growth and mortality default parameters from the regeneration module in PICUS as used in this study

Regeneration parameters	H_1			H_2			H_3			H_4		
	PA	PS	LD	PA	PS	LD	PA	PS	LD	PA	PS	LD
Height growth potential [cm yr^{-1}]	4	5	10	10	10	12	15	15	25	20	25	30
Mortality rate [fraction]	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32	0.32
Min. height growth [cm yr^{-1}]	0.5	1	1	0.5	1	1	1	2	2	1	3	3
Tolerable stress years [yr]	2	1	1	5	3	3	5	3	3	5	3	3

Picea abies (PA), *Pinus sylvestris* (PS) and *Larix decidua* (LD). Height classes: $H_1 = 0\text{--}10\text{ cm}$, $H_2 = 10\text{--}30\text{ cm}$, $H_3 = 30\text{--}80\text{ cm}$, $H_4 = 80\text{--}130\text{ cm}$.

forested slopes comparison of model results with empirical rockfall data is required. To that end no observational rockfall data was available for model validation. However, as a preliminary test published data from an empirical rockfall experiment by Dorren et al. (2005) was compared with results of the similar setting of stand B in Experiment 4. In their experiment Dorren et al. (2005) report that 34% of 100 boulders released down a forested slope (mean boulder size: 0.49 m^3) surpassed 200 m forested zone. This compares well with the 68% boulders stopped on the first 200 m of stand B in year 2005 in Experiment 4 (compare Fig. 8) and supported the hypothesis that the new rockfall module realistically captures major rockfall processes.

To summarize, we are convinced that the coupling of a rockfall module and a dynamic spatially explicit forest patch model bears huge potential to successfully respond to the need for a quantitative assessment tool in rockfall protection forest management (compare e.g., Wehrli, 2005). The vegetation model PICUS used to project forest development can be applied across a wide ecological range of stand and site conditions (Seidl et al., 2005). As a particular asset PICUS offers the advantage of spatially explicit simulation of rockfall activity and vegetation development, a feature, which drastically improves the realism in simulating mountain forest silvicultural concepts and their effect on rockfall protection effects. Quantitative assessment of the rockfall protection effect of forest management over longer time periods is required to provide specific guidelines for management of mountain protection forests. We are convinced that the presented approach is a promising contribution towards that goal.

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Appendix A

See Table A1.

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Importance of public information and perception for managing recreational activities in the Peel-Harvey estuary, Western Australia

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Abstract

Surveys of water recreational activities were conducted in the Peel-Harvey estuary. Channels used by recreationists to gain information about water quality, the perception of water quality and resulting behaviour were investigated. This study showed that personal perception, local knowledge and history, absence of warnings and residency were major factors contributing to risk perception and behaviour in this recreational community. Management strategies should take this information into account to achieve maximal outcomes.

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Keywords: Recreational water; Primary contact; Water quality; Risk perception

1. Introduction

Beach recreational use involves a very large number of people pursuing various leisure activities such as swimming, sunbathing, and sports. Estuarine beaches are frequented by families with young children as they are perceived as less dangerous than those of the open ocean in regard to dangerous animals and waves. However, they are more prone to pollution. Water pollution can have effects upon the benefits of beach use recreation, such as disamenity effects or potential public health risks (Machado and Mourato, 2002). Pollution can affect highly valued water properties such as transparency, taste and odour, as well as contribute to the presence of undesirable floating material. Risk is usually perceived when visible, palatable, or when water clarity is restricted to 1.2 m (Smith et al., 1991). However, high faecal contamination in the Peel-Harvey estuary (Western Australia) as suggested by bacterial indicator level exceeding Australian guidelines by almost a factor of 10 (Lepesteur et al., 2003, 2006) may not create a risk perception amongst beach users (Pendleton et al., 2001). The aim of this study was to

identify the information available to recreationists, their perception, in regard to water quality in the estuary, and their consequent behaviour.

2. Materials and methods

2.1. Site description

The Peel-Harvey estuary is located 70 km south of Perth near the City of Mandurah. Water movement in the Peel-Harvey is caused by tidal currents, wind-driven circulation, density-induced circulation and river flow. The estuary, which is connected to the ocean by a narrow inlet channel at Mandurah and an artificial channel at Dawesville, is a very shallow body of water, more than half the area being less than 0.5 m deep. The Peel Inlet Management Authority (1996) has reported a dramatic improvement in water quality since the opening of the Dawesville channel, with reduced algal and blue-green algae blooms.

There are considerable data on the types and popularity of recreational activities in the Peel-Harvey (Lepesteur et al., 2003). The major recreational pursuits, both active and passive, include fishing, crabbing, prawning, boating, sailing, swimming, water skiing, picnicking and holidaying. Summer holiday periods result in a heavy burden on

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recreation areas and facilities, particularly those centred close to major boat ramps.

The survey location “Mandurah Bridge Beach” is located in the City of Mandurah, at the mouth of the estuary. The beach area is small (about 500 m²) and water quality testing samples were taken close to the recreational users. To reduce short-term variability of indicators (Boehm et al., 2002), duplicate water samples were collected at 3 p.m., on each day the survey was conducted. Samples were collected during and outside the bathing season. They were collected 30 cm below the surface inside the main swimming area. One of the duplicate samples was taken few metres from the “up-stream side” of the swimming enclosure (where the river water enters the swimming area) while the second duplicate was collected few metres from the “downstream side” of the enclosure (where the river water leaves the enclosure). Mandurah Council collects samples monthly in the morning to test for faecal contamination and the Health Department collects samples for toxic algal blooms and nutrients.

Samples were analysed according to the Australian Standard Method (AS 4276.9-1995).

Faecal contamination of the water was evident most of the year with faecal streptococci levels ranging from 61 CFU/100 ml in April to 645 CFU/100 ml in December (Lepesteur et al., 2006). Levels outside the bathing season (April–October) averaged 186 CFU/100 ml despite an increase during the period of high rainfall and river discharge (June), in accordance with the significant increase of microbial concentration following rainfall observed by Crowther et al. (2001).

In contrast, the mean concentration during the bathing season (November–March) was as high as 414 CFU/100 ml. Increased concentrations during the bathing season in recreational areas reflected the impact of recreational users on water quality, as confirmed by lower indicator levels upstream of the main swimming area. These concentrations can be compared with the maximum recommended values of 35 faecal streptococci per 100 ml (NHMRC, 2005; WHO, 2003). Concentrations of 414 CFU/100 ml may result in more than a 16.9% risk of illness per exposure (WHO, 2003) as opposed to risk lower than 6.9% and 1.3% if the concentrations were below 200 and 35 CFU/100 ml.

2.2. Survey

For the purpose of this study, where little was known about perceptions of the water quality in the Peel-Harvey estuary, the perceptual element of the surveys provided insight into to participants perceptions, and how these guide behaviour (Babbie, 2001) (Table 1).

Surveys were conducted on five occasions during summer, the bathing season (November 2002–March 2003) and on three occasions outside the bathing season (April 2002–June 2002) at two recreational sites (Dawes-

Table 1
Survey questions

{Family size/age of members/origin}	• What is your family size including age? • Where do you usually live?
{Activities}	• What activities do you participate in during your stay?
{Perception}	• On a scale of 1–5 of cleanness, how do you rate the water of the Peel-Harvey Inlet?
{Information}	• From where do you get information, if the water is safe?

ville Channel and Mandurah Town). On each occasion, the survey was conducted for 4 h, with participation ranging from 75% to 90% of the recreational users present in the area. The survey focused on the frequency, length and period of visits, on the activities undertaken on the age of the users as well on the public perception of the water quality and relating information available. The surveys were conducted face-to-face, with representatives from each family/group and the researcher filling in the survey form to ensure consistency. A total of 119 families were surveyed, corresponding to 340 individuals (from 0 to 67 years old).

A questionnaire focused on the different sources used by recreationists to gain information on the water quality for these sites. The sources were classified as external (sign, media and social exchange) versus personal observation and perception.

Information obtained from external sources was defined as support of information leading to socially mediated perception of water quality and support of factual knowledge. They included audiovisual as well as printing media and social exchange.

On the other hand, perception of water quality resulting from personal inspection was expected to be influenced by environmental literacy and/or immediate sensation depending on the education level of the user rather than by external channels. Information support classified as ‘others’ (4% of responses) included consulting the local government, Waters and Rivers Commission, rangers, Tourism Bureau or assessing the oceanic intrusion through salt level, demonstrating high literacy skills.

2.3. Follow-up survey

Following the initial survey during the bathing season, participants were contacted by telephone after 2 weeks and asked who among the people present the day of the original survey actually had primary contact activities. For the purpose of this study, primary contact activities were defined as swimming, paddling or playing with/on wet sand.

3. Results and discussion

3.1. Activities in the estuary

Recreational user activities are given in Fig. 1. As one family could claim several activities during their stay, the total exceeded 100%. Primary contact activities (1 and 2) were the most frequently reported activities whatever the season. Over 30% of beach users reported secondary contact activity (3, 4 and 5), with the most frequent, crabbing (activity 3) being reported even outside the crabbing season. On the other hand, fishing was increasingly mentioned during the bathing season. Tertiary contact activities (6, 7 and 8) were significantly more frequent outside the bathing season.

3.2. Public information on water quality

Thirty-eight percent of people surveyed relied on the absence of sign/news in the media as a means of communicating the water quality during the bathing season (Fig. 2). This showed that lack of information, or lack of warning of polluted water quality was perceived as good

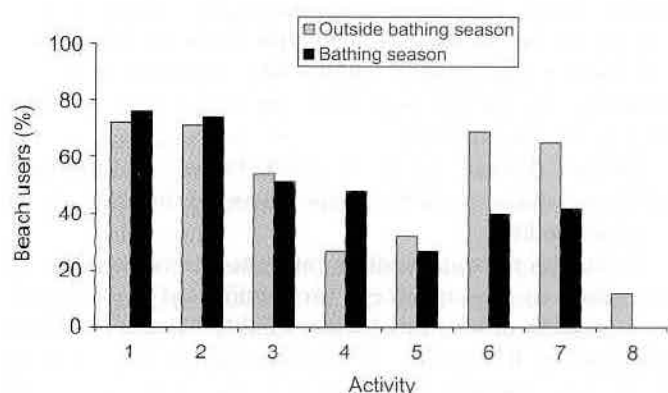


Fig. 1. Water activities in the estuary: (1) swimming/paddling, (2) playing with/on wet sand, (3) crabbing, (4) fishing, (5) boating, (6) playing in the playground, (7) having a picnic/BBQ and (8) walking.

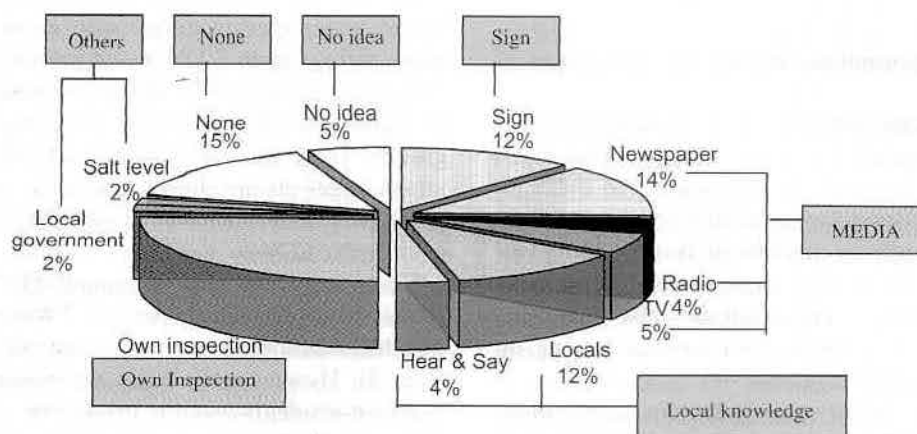


Fig. 2. Channels used by families to gain information about water quality (% of families) during the bathing season.

water quality, indicating the need for a better and more transparent public information strategy.

Almost 25% claimed to be obtaining information from the local paper and news bulletins, which communicate relevant information only when the water quality is so degraded as a result of a spill, a sewage overflow or an algal bloom that any contact with water is potentially dangerous and therefore banned. Public perception was that no news is good news and signifies good water quality. On the other hand, during the bathing season, 17% of families did not receive information from any source, and claimed to have no need for such information. Six percent of respondents had no idea of how they could access information.

The source of information provided to the public indicated seasonal dependency. There was a statistically significant difference, according to season, between the proportions of the population seeking information from the media ($p < 0.0293$, $\alpha = 0.05$), from social exchange ($p < 0.0226$, $\alpha = 0.05$), and from their own inspection ($p < 0.047$, $\alpha = 0.05$). The favoured source of information was the media outside the bathing season, while the importance of social exchange and personal inspection increased during the bathing season. Age did not significantly influence the source of information used, while residency resulted in reliance on social exchange.

3.2.1. Public perception of water quality

Almost a third of the families surveyed relied heavily on their own judgment for assessing water quality (Fig. 2). Understanding and possibly influencing public perception of water quality therefore becomes essential when managing such recreational areas.

As part of the survey, people were asked to rank water quality from poor, to moderate, average, good to excellent, quality on a quality scale from 1 to 5 (1 being excellent and 5 being poor). When asked to rate water quality during the bathing season, 2% of users found this to be of poor quality, 9% of moderate quality, 32% of average quality, 35% of good quality and 22% of excellent quality (Fig. 3). The quality was rated slightly better during the

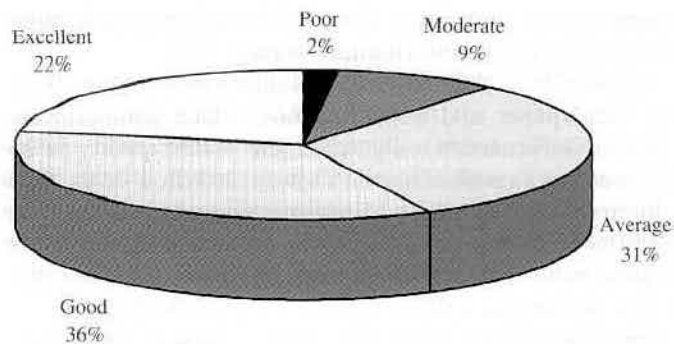


Fig. 3. Water quality rating (% of family) during the bathing season.

bathing season when recreationists tended to rely on their own judgment, rather than outside the bathing season when reliance on media appeared to increase (2.25 ± 0.21 , 95% CI against 2.33 ± 0.28 , 95% CI). However, the difference was not statistically significant ($p < 0.634$, $\alpha = 0.05$).

Smith et al. (1991) reported that a minimum water clarity of 1.2 m, corresponding to a Secchi disk depth of 1.5 m, is required before water is perceived on average as suitable for bathing. Water clarity was variable (ranging from 0.5 to 1.5 m) at the time of the survey due to passing traffic in the waterway and sediment disturbance by the bathers themselves. However, none of the users referred to water clarity as a criterion for assessing water quality. Most users claimed factual knowledge, referring to the history of the estuary, particularly the opening of the Dawesville channel, which allowed more flushing and oceanic intrusion into the estuary. Users perceived the estuary to contain less contamination and to have an improved colour and smell, which corresponds favourably with the improvements revealed in monitoring by management agencies. However, the perception of risk by the public has also presumably changed. The perceived improvement in water quality together with the lack of scientific data about microbial water quality in the system has led to complacency about this issue among users and managers.

3.2.2. Influence of information support on perception of water quality

The study explored the influence of information support on community perception of water quality. The mean ratings ranged from 2 (good) to 2.63 (good to average) depending on the information available to the families. Families who did not rely on any information support had a significantly lower rating than families relying on signs (2.63 against 2, $p < 0.031$). These families also rated the water quality significantly lower than families relying on the other media and social exchange.

People relying on their own judgment, and those generally not seeking information, were more conservative in their rating, rating the water quality as poor (Fig. 4).

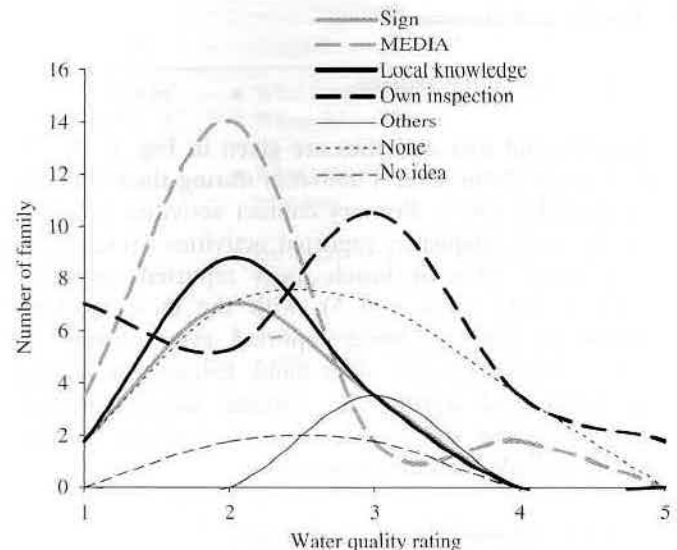


Fig. 4. Influence of channel of information on water quality rating.

Interestingly, the absence of signs about water quality at specific locations could be considered more important than the absence of news on current water quality in any other media. Local experience was also highly valued. People relying on the absence of signs and social exchange gave the best water quality rating (2), demonstrating the influence on public perception of social pressure and absence of warning signs.

People seeking more scientific/factual information (others) perceived water at the surveyed location as of average quality.

There was no statistically significant difference in rating according to season, except for families relying on their own inspection, who rated water quality between excellent and good (1.67) outside the bathing season and between good and average (2.56) during the bathing season ($p < 0.025$).

3.2.3. Influence of age and place of residence on perception of water quality

On average, representatives of each family/group perceived water quality as between good and average, with mean ratings from 2.11 for age group 26–35 and >55 and 2.5 for age group 16–25. However, statistical tests disclosed no significant difference between ratings from different age groups. There was no seasonal variation for individual age group, age group 36–45 excepted, which rated water quality significantly lower in summer compared to the rest of the year (2.86).

Local residents were dominant (70% of respondents). About 50% of residents perceived water quality as good or excellent compared to more than 60% of non-residents (Fig. 5). However, the main difference between residents and non-residents was the propensity of some residents to claim excellent water quality (25% of locals compared to 5% of non-locals).

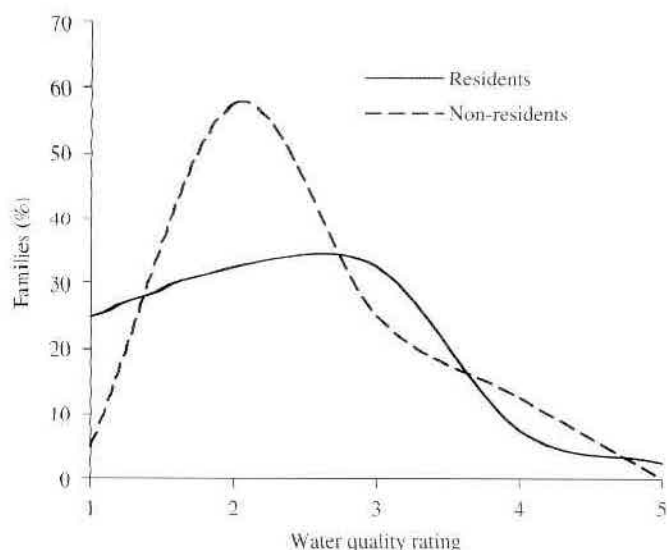


Fig. 5. Influence of residency on water quality perception.

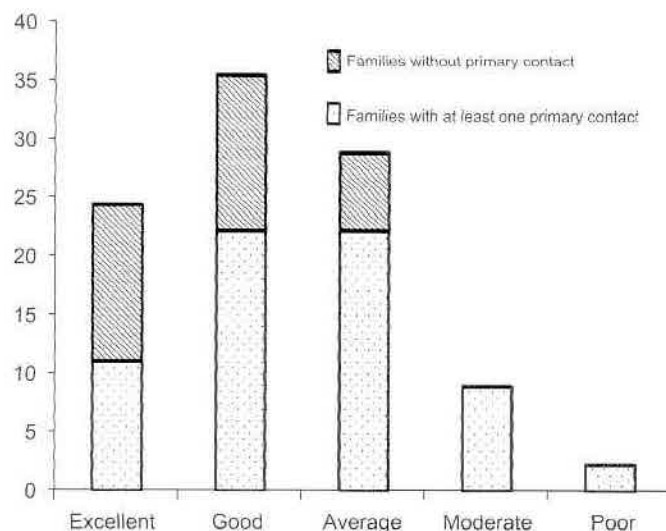


Fig. 6. Influence of water quality perception on recreational behaviour.

3.3. Perception of risk and behaviour

Perceptions reflect personal inclinations (Starbuck and Mezas, 1996). Accessing perceptions provides information on prior beliefs and how they are formed (Ben-Ze'ev, 1993). Additionally, there is a close relationship between perceptions and behaviour (Ivancevich and Matteson, 2002; Lussier and Poulus, 1998; Gibson et al., 2000). Needs and perceptions are regarded as the starting point of human behaviour.

Risk assessors therefore assume that, if given enough information, the public will act in a manner consistent with the relative risks of different activities. However, in many cases people rank risks differently from 'experts' (Slovic, 2000; Kasperson et al., 1988) as a result of subjective judgments, intuition or objective knowledge (Kamrin and Fisher, 1999). People overestimate negligible risks and underestimate significant ones (Slovic et al., 1979), underestimate risks they choose (Lowrance, 1976) and underestimate their own risk compared to those of others (Weinstein, 1989). In this study, more than 20% of respondents perceived there was an environmental risk, as they rated the water quality as poor or moderate. People did not react to their perception of environmental risk as demonstrated in Fig. 6, suggesting that microbial risk was perceived as minimal. Surprisingly, a large proportion of families who perceived the water as excellent or good did not have any one in the family swimming. On the other hand, families who perceived the water as poor or moderate had at least one family member swimming. The overestimation of risk associated with open ocean with the potential presence of dangerous animals, and the false sense of safety in the estuary may have overridden any perception of risk associated with poor water quality.

3.4. Implications for managing recreational areas

This study indicated that the monitoring program in the study area should be modified to reflect variations in bacterial indicator levels and exceedances. Lack of public information about high bacteria levels and associated health risks may be simply due to an inadequate monitoring program.

This work also provided insights into participants' channels of information, their perceptions, and how these guide behaviour. Pendleton et al. (2001) reported that residents of Los Angeles County tend to hold perceptions of marine water quality at odds with data on bacteriological measures of water quality collected by local sanitation districts despite education campaigns, and suggested that perception of coastal water quality may be less influenced by coastal education campaigns than by media and other factors. On the other hand, McDaniels et al. (1998) reported that residents of a watershed of British Columbia perceived water quality as worse than was indicated by technical reports. The present study showed that social exchange, perception of environmental conditions and personal impressions were often more significant than factual environmental information, as previously reported by Szagun and Pavlov (1995).

Previous studies have shown that environmental concerns (here the perception of water quality) depend on social and physical characteristics such as size of neighbourhood, length of residence and educational level (Syme et al., 2002). Moreover, Olli et al. (2001) reported the social context as the most important variable for environmental behaviour and perception while Vorkinn and Riese (2001) identified place attachment as a more important variable than sociodemographic variables for environmental perception in a local context. This study illustrated the importance of local history, as residents were referring to improvement in water quality (smell and clarity) when rating the current water quality.

This study also pointed out the need for signage and environmental education to increase awareness and understanding of water quality issues amongst beach users. Signs should be designed to comply with the user cognitive capabilities and expectations. Beehler et al. (2001) suggested that risk messages posed as formal written advisories could be distributed with fishing licences, presenting scientifically based information, about subjects not often perceived as a risky behaviour to recreational users or their children. Because of this linkage between parents, children and recreational behaviour, it would be important to consider how risk communication messages are constructed (Beehler et al., 2002). Common schemas for information order have been identified by Smith-Jackson and Hall (2002); however, previous studies indicated that, while increasing the understanding of risk, information might not modify behaviour (Orams, 1997; Tubb, 2003).

While focusing on the impact of place of residence, age and information support, this study emphasised aggregate level data and minimised individual differences. It also considered the population as homogenous in terms of education level and socioeconomic background. Nevertheless, findings from this study suggested underlying processes that may explain the variability in perception. Szagun and Pavlov (1995) reported that an individual's perception of risk was often socially mediated because it is derived from information presented in the mass media and environmental curricula rather than any real feeling of the environment. The claim of relying on one's "personal inspection" would therefore be flawed, and measuring perceptions would provide a more indicative measure of environmental literacy than factual knowledge and/or feeling. Therefore, differences in socioeconomic status, education level, place of residence and ethnicity may have resulted in significant differences in judgement (Weber et al., 2000).

4. Conclusion

Primary contact activities were most frequently reported activities amongst beach users in the Peel-Harvey estuary. Whatever their age, most recreationists relied on (1) media and signs, (2) their own perception and (3) local knowledge, to gain information about water quality. But the importance of the different information channels varied according to season and place of residency.

The reliance on lack of pollution warning through signs and media in particular indicated the need for a better and more transparent public information strategy.

Forty-two percent of beach users perceived that there was an environmental risk as they rated water quality as poor to average. However, this risk was clearly underestimated as there is no behavioural action resulting from this risk perception.

This study emphasised the need for more work on education/awareness programmes targeting residents for changing their perception and their tendency to complacency.

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Advanced oxidation treatment of pulp mill effluent for TOC and toxicity removals

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Abstract

Pulp mill effluent was treated by different advanced oxidation processes (AOPs) consisting of UV, UV/H₂O₂, TiO₂-assisted photo-catalysis (UV/TiO₂) and UV/H₂O₂/TiO₂ in lab-scale reactors for total organic carbon (TOC) and toxicity removals. Effects of some operating parameters such as the initial pH, oxidant and catalyst concentrations on TOC and toxicity removals were investigated. Almost every method resulted in some degree of TOC and toxicity removal from the pulp mill effluent. However, the TiO₂-assisted photo-catalysis (UV/TiO₂) resulted in the highest TOC and toxicity removals under alkaline conditions when compared with the other AOPs tested. Approximately, 79.6% TOC and 94% toxicity removals were obtained by the TiO₂-assisted photo-catalysis (UV/TiO₂) with a titanium dioxide concentration of 0.75 g l⁻¹ at pH 11 within 60 min.

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Keywords: Advanced oxidation process (AOPs); UV/TiO₂; UV/H₂O₂/TiO₂; Pulp mill effluent

1. Introduction

Effluents of the pulp and paper industry contain a number of toxic compounds and may cause deleterious environmental impacts upon direct discharge to receiving waters. Pulping processes utilize large amounts of water, which reappear in the form of an effluent. The most significant sources of pollution in pulp and paper industry are wood preparation, pulping, pulp washing, bleaching and coating operations. Among the various processing steps, pulping generates a high-strength wastewater containing toxic chemicals such as phenolics (Pokhrel and Viraraghavan, 2004).

Three main groups of organic compounds present in paper industry are: (a) starch degradation products, such as saccharides or carboxylic acids, (b) phenolic compounds arising from lignin and (c) other pollutants that may be present in the fresh waters such as surfactants (Amat et al., 2005). Effluents of paper industry contain suspended solids, chemical oxygen demand (COD), toxicity, color,

AOX compounds and high concentration of nutrients that cause eutrophication in receiving water (Poole et al., 1978; Pokhrel and Viraraghavan, 2004).

Since some of the contaminants in pulp and paper industry effluents are non-biodegradable, conventional biological treatment processes are not sufficient for treatment. The extent of toxicity, total organic carbon (TOC) and color removal by conventional biological treatment vary depending on the pulping process used. In order to meet increasingly stringent discharge limits, pulp mills are forced to adopt technologically advanced treatment systems. Organic compounds such as chlorophenols are not fully degraded by biological processes, which require advanced oxidation after biological treatment to reduce refractory organics and toxicity of the pulp mill wastewater. The number and position of chlorine groups on the aromatic ring strongly affects biodegradability and toxicity of chlorinated compounds (Annachhatre and Gheewala, 1996). Different biological tests were used for toxicity assessment of individual chemicals or complex effluents (Strotmann et al., 1993; Farre and Barcelo, 2003). One of the recently developed toxicity assessment method is the 'resazurin assay' which is relatively simple, inexpen-

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sive and rapid (Brouwer, 1991; Strotmann et al., 1993). The basic principle of the method is the measurement of percent inhibition on dehydrogenase activity of bacteria in the presence of toxic compounds. Toxicity values obtained with the resazurin assay are comparable to those obtained with the more commonly used biological methods such as *Daphnia magna*, and MicrotoxTM (Farre and Barcelo, 2003).

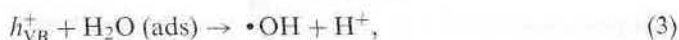
Advanced oxidation processes (AOPs) were developed and used as potentially powerful methods capable of transforming the pollutants into harmless substances (Esplugas et al., 1994). AOPs are based on the generation of very reactive non-selective transient oxidizing species such as the hydroxyl radicals ($\text{OH}^\bullet$) which were identified as the dominant oxidizing species (Masten and Davies, 1994). For effective oxidations of refractory organic compounds, the hydroxyl radicals must be generated continuously in situ through chemical or photochemical reactions due to their instability. Generation of $\text{OH}^\bullet$ radicals is commonly accelerated by combining some oxidizing agents such as ozone (O_3), hydrogen peroxide (H_2O_2), UV radiation, ferrous and ferric salts (Fe^{2+} and Fe^{3+}) and catalysts such as TiO_2 . Among those methods, UV plus hydrogen peroxide (UV/ H_2O_2), Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$), photo-Fenton (UV/ $\text{H}_2\text{O}_2/\text{Fe}^{2+}$), TiO_2 -assisted photo-catalysis (UV/ TiO_2), UV/ $\text{H}_2\text{O}_2/\text{TiO}_2$, $\text{O}_3/\text{H}_2\text{O}_2$ and O_3/UV hold the greatest promise for detoxification and mineralization of pollutants. Among these processes photo-catalytic systems such as combination of a semiconductor (TiO_2 , ZnO) with UV light is a very promising technique. Due to a faster electron transfer to molecular oxygen, TiO_2 was found to be more efficient than ZnO for photo-catalytic degradation of pollutants (Daneshvar et al., 2004).

Semiconductor materials used in environmental applications include titanium oxide (TiO_2), strontium titanium trioxide and zinc oxide (ZnO). TiO_2 is generally preferred in commercial AOP applications because of its high level of photoconductivity, availability, low level of toxicity, low cost and relatively high chemical stability (Konstantinou and Albanis, 2004). Photo-catalytic degradation of recalcitrant organic contaminants in the presence of TiO_2 has been recently investigated (Carraway et al., 1994; Maugans and Akgerman, 1997), since a large number of aliphatic and aromatic compounds can be mineralized by UV/ TiO_2 treatment under suitable conditions. The process is initiated upon UV irradiation of the semiconductor with the formation of high-energy electron/hole pairs by exciting an electron from the valance band (VB) to the conduction band (CB):



The highly oxidative $h\nu_{\text{VB}}^+$ ($E_0 = 2.8 \text{ V}$) may directly react with the surface-sorbed organic molecules to form R^+ or indirectly via the formation of OH radicals (Gimenez et al., 1997; Konstantinou and Albanis, 2004). The reaction of the photo-generated holes with water molecules and

hydroxyl ions adsorbed on the surface of TiO_2 yields formation of hydroxyl radicals (San et al., 2002; Gomes da Silva and Faria, 2003):



The resulting hydroxyl radicals are strong oxidizing agents and can oxidize most of the organic compounds (Maurino et al., 1999). Major drawback of photo-catalytic processes is the need to remove the catalyst after treatment and the limited surface area of semiconductors.

The major objective of this study is to investigate the performance of different advanced oxidation methods and their combinations for toxicity and TOC removal from paper mill effluent. Direct photolysis (UV), hydrogen peroxide with UV, TiO_2 -assisted photo-catalysis (UV/ TiO_2) and UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$ treatments were employed at different pH (3–11), H_2O_2 doses (5–100 mM), TiO_2 doses (0.25–2 g l⁻¹ or 3.125–25 mM) for the treatment of pulp mill effluent.

2. Materials and methods

2.1. Characterization of the pulp mill effluent

Wastewater used in this study was obtained from biological wastewater treatment plant of a pulp and paper manufacturing company located in Izmir, Turkey. Composition of the pulp mill wastewater used in this study is presented in Table 1. Low BOD/COD ratio of 0.41 indicated low biodegradability of the organic compounds present in the wastewater requiring advanced treatment.

2.2. Materials

The titanium dioxide (Degussa P-25) was composed of 80% anatase and 20% rutile with a BET surface area of 50 m² g⁻¹ and average particle size of 30 nm. Hydrogen peroxide solution (35%, w/w, Merck) was diluted with deionized water before treatment. The pH of aqueous solutions was adjusted using dilute (1%) sodium hydroxide or sulfuric acid solutions. All solutions were prepared by using distilled water.

Table 1
Composition of the pulp mill effluent used in this study

Parameters		Parameters	
pH	7.08	Phenol (mg l ⁻¹)	0.755
COD (mg l ⁻¹)	592	AOX (mg l ⁻¹)	1.936
BOD (mg l ⁻¹)	240	Conductivity (μmhos/cm)	979
TOC (mg l ⁻¹)	171	UV ₂₅₄ (m ⁻¹)	0.479

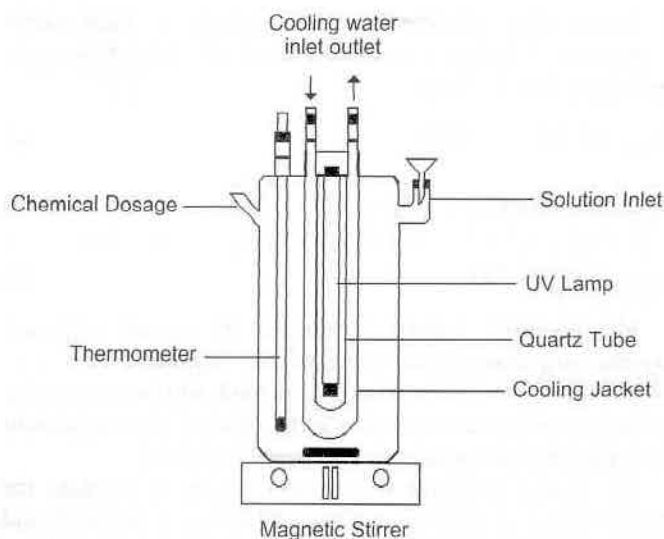


Fig. 1. A schematic diagram of experimental set-up for the UV reactor.

2.3. Reactor configurations

Fig. 1 depicts a schematic diagram of the laboratory-scale photochemical reactor used in UV oxidations. All photo-oxidation experiments were performed in the completely mixed, batch, cylindrical photo-reactor made of glass with a total volume of 2.2 l. The reactor was covered with an aluminum foil to avoid any light leakage to the outside. The reactor was placed on a magnetic stirrer and contained inlets for feeding the reactants, and ports for sample removal and temperature measurements. The UV irradiation source was a 16 W low-pressure mercury vapor lamp (maximum emission at 254 nm) placed in a quartz tube. The intensity of the UV radiation was measured using the ferrioxalate actinometry method and found to be 4.98×10^{-6} E/s (San et al., 2002). The lamp was surrounded with a water-cooling jacket to remove the heat produced by the lamp and to maintain a constant temperature. The lamp tube was immersed in aqueous solution.

2.4. Experimental procedure

Chemical treatment with TiO_2 was carried out by using different TiO_2 doses at a pH of 11. The conventional jar tests were started by adding different amounts of TiO_2 to pH-adjusted wastewater samples. After pH adjustment and chemical addition, wastewater was mixed rapidly for 60 min at 45 rpm. Samples were withdrawn for analysis at the end of the mixing period.

$\text{TiO}_2/\text{H}_2\text{O}_2$ experiments were carried out at room temperature using different hydrogen peroxide and a constant titanium dioxide concentration of 0.75 g l^{-1} at a constant pH value of 7. Desired amounts of hydrogen peroxide and titanium dioxide were added to pH-adjusted wastewater samples. After pH adjustment and oxidant/catalyst addition, wastewater was mixed rapidly for 60 min

at 45 rpm. Samples were withdrawn for analysis at the end of the mixing period.

In advanced oxidation treatments with UV, the pH was manually adjusted to a desired value using dilute sulfuric acid or sodium hydroxide. Then, predetermined amounts of chemicals (H_2O_2 or/and TiO_2) were injected to the reactor at the beginning of each experiment. In experiments using UV/ TiO_2 and UV/ $\text{TiO}_2/\text{H}_2\text{O}_2$ treatment, desired amounts of titanium dioxide was injected into the reactor after pH adjustment at the beginning of each experiment. Titanium dioxide was mixed well with wastewater before the addition of hydrogen peroxide solution. The experiments were started by turning the UV lamp on after the addition of the reagents. All experiments were carried out in batch mode. Two experiments in every set were repeated twice to test the reproducibility of the data. Since the difference in results was less than 5% the other experiments were not repeated.

2.5. Analytical methods

Samples were removed from the reactors at pre-determined time intervals for immediate analysis of TOC and toxicity. The temperature of the solution was kept constant at $25 \pm 2^\circ\text{C}$ throughout the experiments. After TiO_2 oxidation, reactor was washed with concentrated HNO_3 solution followed by distilled water. The aqueous samples were centrifuged before analysis to remove TiO_2 agglomerates. A bench scale pH meter (NEL pH meter 890) was used for pH measurements. TOC analyses were done using a DOHRMAN DC 190 TOC analyzer. A conductivity meter (YSI 33) was used for conductivity measurements. The UV_{254} is a measure of quantity of unsaturated bonds in wastewater and is an effective parameter to indicating the efficiency of organic matter decomposition. Soluble COD and other wastewater parameters presented in Table 1 were determined using the standard methods of analysis (APHA, 2005).

Resazurin reduction method was used to determine the toxicity of the feed and effluent wastewater (Brouwer, 1991; Strotmann et al., 1993). The test organisms (washed activated sludge) to be subjected to the toxic feed and effluent wastewater were cultivated on nutrient broth and were used for determination of the toxicity of wastewater samples. The test cultures were transferred everyday to fresh medium to keep the sludge age constant during the course of toxicity measurements. In the presence of active bacterial culture, as a result of dehydrogenase enzyme activity, resazurin changes color from blue to pink forming the reduced compound resorufin. Therefore, the color of the resazurin solution is an indicator of bacterial activity. A spectrometer (Novaspec II, Pharmacia Biotech) was used at 610 nm for determination of the color intensity of the resazurin added samples. In order to decompose residual H_2O_2 to avoid interference with the toxicity measurement, the samples containing H_2O_2 were treated with MnO_2 powder (50 mg/25 ml sample) and were centrifuged and

filtered through 0.45 μm Millipore membranes to remove MnO_2 .

3. Results and discussion

3.1. UV/ TiO_2 treatment

In order to investigate the effects of both pH and TiO_2 concentrations on TOC and toxicity removals, a number of experiments were carried out with UV/ TiO_2 treatment.

3.1.1. Effects of initial pH

Acidic (pH 3), neutral (pH 7) and alkaline (pH 11) pH levels were used in order to determine the most suitable pH for UV/ TiO_2 treatment in terms of percent TOC and toxicity removals from the pulp mill effluent. TiO_2 concentration was constant at 1 g l^{-1} and the reaction time was 60 min throughout this set of experiments. Fig. 2 shows variation of percent TOC and toxicity removals at different pH levels. Percent TOC and toxicity removals from the wastewater increased with increasing pH yielding 31.6% TOC and 55% toxicity removals at initial pH of 3; 30.1% TOC and 78.3% toxicity removals at pH 7 and 39.6% TOC and 68.9% toxicity removals at pH 11 at the end of 60 min, which was selected as the most suitable pH although the highest toxicity removal (78.3%) was obtained at pH 7. Decomposition of pulp mill effluent by photocatalytic treatment was represented with the first-order kinetics by other investigators (Chang et al., 2004). Table 2 summarizes the calculated apparent first-order rate constants for removal of TOC and toxicity using UV/ TiO_2 treatment for the first 5 min since the reaction was almost completed within 5 min. The results clearly indicated that decreasing initial pH adversely affected the apparent first order reaction rate constant (k_1) which decreased from 0.077 to 0.027 min^{-1} when the initial pH was decreased from 11 to 3 for TOC removal. High TOC removals at alkaline pH 11 can be explained by the increased amount of $\cdot\text{OH}$ ions on the surface of TiO_2 . As the pH increased $\cdot\text{OH}$ ions were combined with $h\nu_{\text{B}+}$ to produce more

$\cdot\text{OH}$ radicals (Poulios and Tsachpinis, 1999). Percent toxicity removal at the end of 60 min was higher at pH 7 as compared to the other pH levels tested.

3.1.2. Effects of initial TiO_2 dose

A set of experiments with UV/ TiO_2 were carried out with variable TiO_2 concentration at pH 11. Fig. 3 depicts variation of percent TOC and toxicity removals with the TiO_2 dose at a constant initial pH of 11 and titanium dioxide doses of between 0.25 and 2 g l^{-1} at the end of 60 min reaction time. After addition of TiO_2 and turning on the UV lamp, a fast decrease in TOC was observed within 5 min. TOC removal after 5 min of reaction time was negligible at all TiO_2 concentrations and the effluent pH remained almost constant. The reaction rate for the UV/ TiO_2 treatment was reported to be fast yielding complete oxidation within a short period of time (Lanzalunga and Bietti, 2000; Tanaka et al., 2000). The reason for negligible TOC removal after the first 5 min may be because of adsorption of the organic matter on the catalyst surface to form a layer hindering degradation by reducing the O_2 supply to the surface of TiO_2 . It is well known that high TiO_2 concentrations may inhibit the photo-catalytic oxidations (Legrini et al., 1993; Chen and Ray, 1998). Percent TOC and toxicity removals increased with TiO_2 concentration up to 0.75 g l^{-1} and then decreased with further increases in TiO_2 . Excessive TiO_2 dosages above the optimum level cause a shadowing effect which interferes

Table 2

Apparent first-order rate constants (k_1) for TOC and toxicity removals from the pulp mill effluent by UV/ TiO_2 treatment at different pH values. (TiO_2 1 g l^{-1})

UV/ TiO_2 treatment	k_1 (min^{-1})	
	TOC	Toxicity
pH 3	0.027	0.023
pH 7	0.064	0.129
pH 11	0.077	0.156

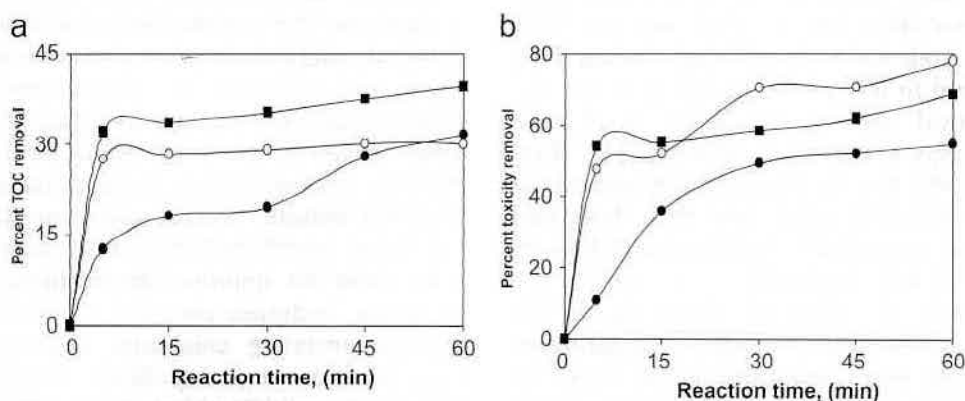


Fig. 2. Variations of (a) percent TOC, (b) percent toxicity removals with the initial pH in UV/ TiO_2 treatment at 1 g l^{-1} TiO_2 . pH: ● 3, ○ 7, ■ 11.

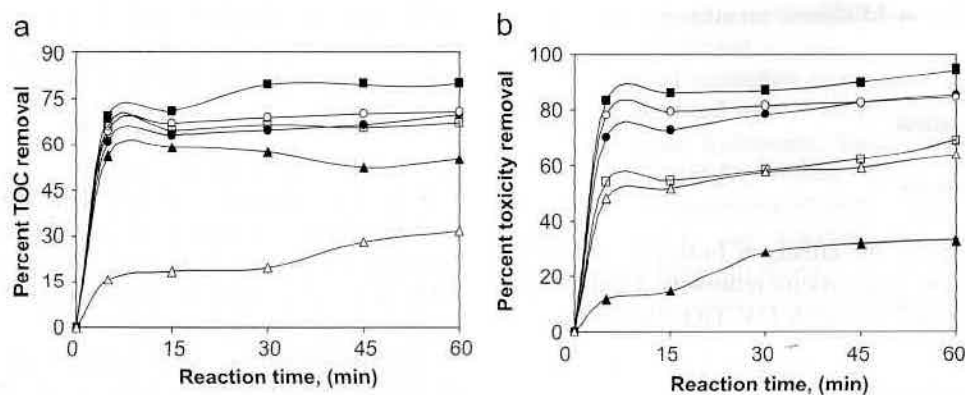


Fig. 3. Variations of (a) percent TOC, (b) percent toxicity removals with initial TiO_2 concentration in UV/ TiO_2 treatment at pH 11. TiO_2 (g l^{-1}): ● 0.25, ○ 0.50, ■ 0.75, □ 1, ▲ 2, △ 0.

Table 3

Apparent first-order rate constants (k_1) for TOC and toxicity removals from the pulp mill effluent by UV/ TiO_2 treatment at different TiO_2 concentrations. (pH 11)

TiO_2 concentration (g l^{-1})	k_1 (min^{-1})	
	TOC	Toxicity
0 (UV only)	0.034	0.132
0.25	0.188	0.240
0.5	0.204	0.305
0.75	0.233	0.359
1	0.215	0.156
2	0.165	0.025

with the transmission of UV light, preventing formation of electron-hole pairs and, therefore, yielding low TOC and toxicity removals. TiO_2 addition to the UV system improved both TOC and toxicity removals considerably as compared to UV treatment alone even at low TiO_2 concentrations. When UV treatment was used alone without TiO_2 , only 31.6% of TOC and 63.7% of toxicity were removed within 60 min of reaction time (Fig. 3). The results indicated that the UV/ TiO_2 treatment was quite effective with 0.75 g l^{-1} TiO_2 at pH 11 resulting in 79.6% TOC and 94.2% toxicity removals. As presented in Table 3, the apparent first-order rate constant (k_1) for TOC removal increased from 0.034 to 0.233 min^{-1} when TiO_2 was increased from 0 to 0.75 g l^{-1} . The rate constant (k_1) for toxicity removal also increased to 0.132 and 0.359 min^{-1} when only UV and UV with 0.75 g l^{-1} TiO_2 were used, respectively. Our results are much better than those reported in literature since only 50% TOC and toxicity removals were reported by Yeber et al (2000) with 42 mg l^{-1} TiO_2 in UV/ TiO_2 treatment.

In order to clarify the effect of photolysis on the treatment of pulp mill effluent, a number of experiments with titanium dioxide were performed in the dark. As presented in Fig. 4, percent removals obtained with TiO_2 in the dark were lower than those of TiO_2/UV treatment •OH

ion formation in the presence of UV. The results indicated that TOC removal in UV/ TiO_2 treatment was not only due to adsorption of pollutants on TiO_2 surfaces, but by photocatalytic degradation. The fast oxidation of the organic matter (TOC removal) in UV/ TiO_2 treatment during the first 5 min was by means of heterogeneous photo-catalysis and direct photolysis. This removal mechanism was mentioned by Machado et al. (2000) for the treatment of the peroxy-formic acid-lignin and biphenyl-lignin compounds. Addition of UV irradiation also significantly enhanced the toxicity removals obtained by TiO_2 in the dark. Low percent toxicity removal in the presence of UV at TiO_2 dose of 2 g l^{-1} may be due to formation of toxic end products.

3.2. Treatment by UV/ H_2O_2 / TiO_2

Titanium dioxide (TiO_2) is known to be more effective due to the formation of electron-hole pairs under illumination with UV light. Nevertheless, recombination of electrons and holes inhibit the photo-catalytic reaction process as mentioned in UV/ TiO_2 treatment. Some oxidants (oxygen, hydrogen peroxide, oxyhalogens) improve the performance of UV/ TiO_2 treatment by capturing the electrons ejected from TiO_2 and, therefore, reducing the probability of recombination of e^- and h^+_{VB} , yielding higher available number and the survival time of h^+_{VB} (Irmak et al., 2004). Recently, some investigators examined the effect of H_2O_2 on oxidation of organic pollutants, such as chlorophenols and atrazine mediated by TiO_2 (Wong and Chu, 2003). Addition of small amounts of hydrogen peroxide can significantly increase the generation rate of hydroxyl radicals, thereby enhancing the oxidation efficiencies of organic pollutants mediated by TiO_2 .

In order to improve the performance of UV/ TiO_2 treatment, hydrogen peroxide was added using the most suitable operating conditions determined. Experiments were carried out using H_2O_2 concentrations ranging between 5 and 100 mM in the presence and absence of UV light at an optimum TiO_2 concentration of 0.75 g l^{-1} .

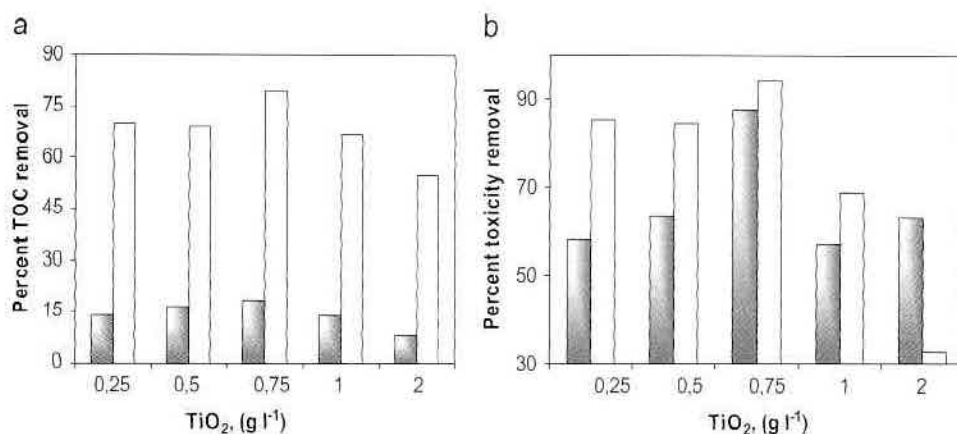


Fig. 4. Variations of (a) percent TOC, (b) toxicity removals with TiO_2 concentrations in UV/ TiO_2 treatment at pH 11: (■) in the absence of light and (□) in the presence of light.

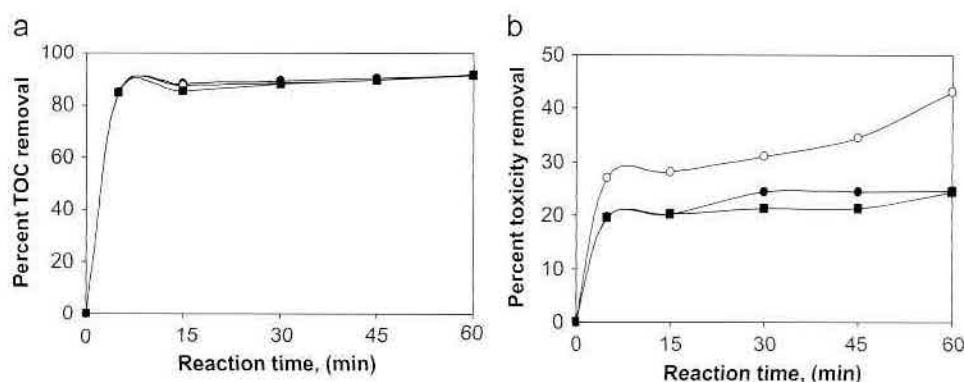


Fig. 5. Variations of (a) percent TOC, (b) toxicity removals with the initial pH in UV/ H_2O_2 / TiO_2 treatment at 0.75 g l^{-1} TiO_2 and 50 mM H_2O_2 , pH: ● 3, ○ 7, ■ 11.

3.2.1. Effects of initial pH

Fig. 5 depicts variation of percent toxicity and TOC removals with the initial pH at a constant hydrogen peroxide and TiO_2 concentrations of 50 mM and 0.75 g l^{-1} , respectively, at the end of 60 min reaction time. Percent toxicity removals were low under acidic and alkaline conditions, yielding a maximum toxicity removal of 47% at pH 7. However, percent TOC removals were not affected from pH changes, yielding 84.5–84.8% TOC removals at all pH levels tested. The apparent first-order rate constants for TOC and toxicity removals were 0.377 and 0.063 min^{-1} , respectively, at pH 7 (Table 4). Since the maximum toxicity removal was obtained at pH 7 and TOC removals were nearly the same at all pH values, further experiments with UV/ H_2O_2 / TiO_2 were carried out at pH 7. In another study, pH 7 was also found to be the optimum for the treatment of pesticides containing wastewater by UV/ H_2O_2 / TiO_2 (Doong and Chang, 1997).

3.2.2. Effects of initial H_2O_2 dose

A set of experiments were carried out with variable H_2O_2 concentrations between 5 and 100 mM at a pH of 7 and

Table 4

Apparent first-order rate constants (k_1) for TOC and toxicity removals from the pulp mill effluent by UV/ H_2O_2 / TiO_2 treatment at different pH values (TiO_2 0.75 g l^{-1} , H_2O_2 50 mM)

UV H_2O_2 / TiO_2 treatment	k_1 (min^{-1})	
	TOC	Toxicity
pH 3	0.374	0.044
pH 7	0.378	0.063
pH 11	0.373	0.043

constant titanium dioxide concentration of 0.75 g l^{-1} in the presence and absence of UV light. Fig. 6 depicts variation of percent toxicity and TOC removals with the H_2O_2 concentration at constant initial pH of 7 in the presence of UV light. Addition of H_2O_2 to the UV/ TiO_2 system improved TOC removal considerably as compared to UV/ TiO_2 treatment alone even at low H_2O_2 concentrations. Percent TOC removal increased with H_2O_2 concentration up to 75 mM and then decreased with further increases in

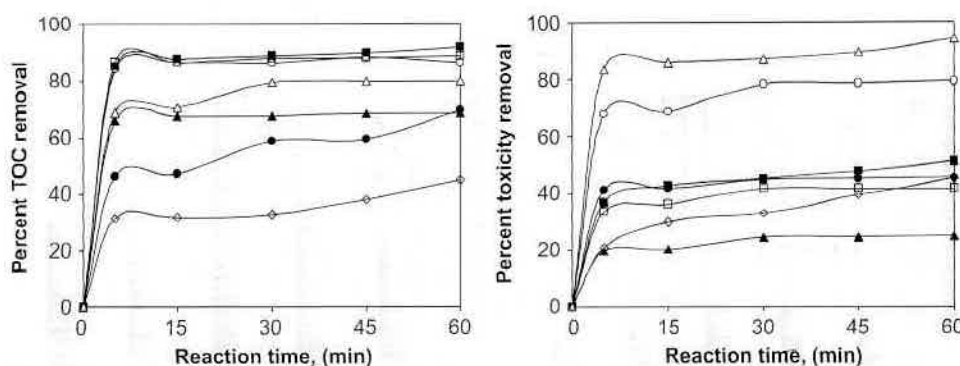


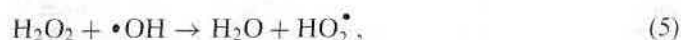
Fig. 6. Variations of (a) percent TOC, (b) percent toxicity removals with initial H_2O_2 concentration in UV/ H_2O_2 / TiO_2 treatment at 0.75 g l^{-1} TiO_2 and pH 7. H_2O_2 (mM): $\triangle$, 0, $\bullet$, 5, $\circ$, 25, $\blacksquare$, 50, $\square$, 75, $\blacktriangle$, 100, $\diamond$ TiO_2 0, H_2O_2 25 mM.

Table 5

Apparent first-order rate constants (k_1) for TOC and toxicity removals from the pulp mill effluent by UV/ H_2O_2 / TiO_2 treatment at different H_2O_2 concentrations (pH 7, TiO_2 0.75 g l^{-1})

UV/ H_2O_2 / TiO_2 treatment	k_1 (min^{-1})	
	TOC	Toxicity
UV only	0.034	0.132
UV/ H_2O_2 (25 mM)	0.076	0.047
UV/ TiO_2 (0.75 g l^{-1})	0.233	0.359
UV/ H_2O_2 / TiO_2 (5 mM)	0.124	0.106
UV/ H_2O_2 / TiO_2 (25 mM)	0.368	0.227
UV/ H_2O_2 / TiO_2 (50 mM)	0.378	0.091
UV/ H_2O_2 / TiO_2 (75 mM)	0.406	0.082
UV/ H_2O_2 / TiO_2 (100 mM)	0.215	0.044

H_2O_2 . As presented in Table 5, the apparent first-order rate constant (k_1) for TOC removal decreased from 0.406 to 0.214 min^{-1} when the concentration of H_2O_2 was increased from 75 to 100 mM. At high H_2O_2 concentrations, photocatalytic oxidation was inhibited by the reactions of excess H_2O_2 with $\bullet\text{OH}$ radicals and $\text{h}\nu_{\text{VB}}^+$ (Tanaka et al., 2000; Konstantinou and Albanis, 2004).



However, addition of H_2O_2 to UV/ TiO_2 system did not enhance toxicity removal. Toxicity removal decreased from 94.2% to nearly 50% with the addition of H_2O_2 to UV/ TiO_2 treatment. Moreover, the first-order rate constant (k_1) for toxicity removal decreased from 0.359 to 0.044 min^{-1} with the addition of 100 mM H_2O_2 to UV/ TiO_2 treatment (Table 5). Therefore, the most suitable hydrogen peroxide concentration was selected to be 25 mM on the basis of the

highest first-order rate constants (0.368 min^{-1} for TOC and 0.227 min^{-1} for toxicity).

In order to clarify the effect of photolysis on the treatment of pulp mill effluent, a number of experiments with TiO_2 and H_2O_2 were performed in the dark. As presented in Fig. 7, when the pulp mill effluent was treated with the TiO_2 and H_2O_2 in the dark for 60 min, only 67.8% TOC and 79.9% toxicity were removed without UV irradiation. The results indicated that TOC removal (84.1%) in UV/ H_2O_2 / TiO_2 treatment was not only due to adsorption on TiO_2 surfaces, but by the photo-catalytic degradation. Addition of irradiation (UV) did not enhance toxicity removals (79.1%) obtained from TiO_2 experiments in the dark (79.9%). The results indicated that toxicity of intermediate products resulted in UV/ TiO_2 / H_2O_2 treatment was higher than those in TiO_2 / H_2O_2 treatment.

In order to further clarify the role of TiO_2 in advanced oxidation of the pulp mill effluent, the experiment with 25 mM H_2O_2 at pH 7 was also performed only with UV/ H_2O_2 treatment without TiO_2 . Percent toxicity and TOC removals were 44% and 45%, respectively, for the UV/ H_2O_2 treatment (Fig. 6). Addition of TiO_2 to the UV/ H_2O_2 system improved both toxicity and TOC removals considerably as compared to UV/ H_2O_2 treatment. Moreover, the apparent first-order rate constant (k_1) for toxicity removal increased from 0.047 to 0.227 min^{-1} with the addition of 25 mM TiO_2 to UV/ H_2O_2 treatment (Table 5). As a result, 84.1% TOC and 79.1% toxicity removals were obtained in 60 min with UV/ TiO_2 / H_2O_2 treatment when 25 mM H_2O_2 and 0.75 g l^{-1} TiO_2 were used at pH 7.

4. Conclusions

TOC and toxicity removals from a pulp mill effluent were investigated by using different advanced oxidation methods (AOPs). Effects of pH and concentrations of the reagents were investigated for each treatment method tested and the most suitable pH and oxidant concentrations were determined. Peak performances of each treatment method were compared for TOC and toxicity

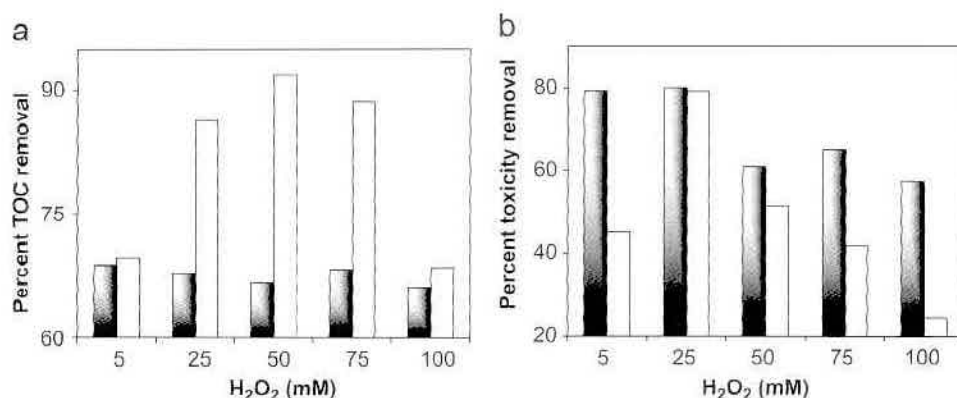


Fig. 7. Variations of (a) percent TOC, (b) percent toxicity removals with H_2O_2 concentrations in UV/ H_2O_2 / TiO_2 treatment at a 0.75 g l^{-1} TiO_2 and pH 7; (■) in the absence of light and (□) in the presence of light.

removals. Either TiO_2 -assisted photo-catalysis (UV/ TiO_2) or UV/ H_2O_2 / TiO_2 treatment can be used to obtain high percent TOC removals. However, TiO_2 -assisted photo-catalysis treatment seems to be more advantageous yielding higher toxicity removal as compared with UV/ H_2O_2 / TiO_2 . Treatment by TiO_2 -assisted photo-catalysis yielded high toxicity (94%) and TOC (79.6%) removals at a pH of 11 with 0.75 g l^{-1} TiO_2 after 60 min of treatment.

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Nonlinear time series analysis of ground-level ozone dynamics in Southern Taiwan

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Abstract

The ozone pollution at ground level in rural and urban areas has been a long-standing problem in the world. This paper focuses on estimating self-affined nature of nonlinearity of ground-level peak ozone time series, which is analyzed by two nonlinear fractal statistical methods, including *R/S* analysis and BDS test. To explore the underlying structure of ozone observations at ground level and improve the forecasting capacity in urban region, practical implementation was assessed by a case study via collecting and analyzing the monitoring data at Chaiohou and Zenwu in the Kaohsiung metropolitan region, Taiwan. Based on *R/S* analysis, the time series can be identified as persistent and long-memory processes with Hurst exponents of both about 0.75. In addition, the *V* statistics specifies possible fluctuation cycle lengths of 32, 170, and 420 day simultaneously. Such results are consistent with the regional meteorological conditions leading to help characterize the regional scale ozone behavioral trend. Furthermore, the BDS test results confirm a strong nonlinearity of both time series associated with these two cities. Yet in both cases, nonlinearity implies chaos. The *R/S* analysis and BDS test provide strong evidence for nonlinearity and fractality of ozone time series due to noisy chaos, and we could not rule out the possibility of deterministic chaos in tropospheric ozone system.

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1. Introduction

Ambient ozone has been proved to be a serious air pollution problem for many industrialized countries. It not only causes detrimental human health problem (Larsen et al., 1991; Spektor et al., 1991; Kinney et al., 1996; Freijer et al., 2002) but also makes huge damage to vegetation, architecture, and ecological system (Laurance, 1998). The agriculture damage is estimated to exceed several billion dollars annually (Larsen and Heck, 1984; Fernandez-Bayon et al., 1993; Slaughter et al., 1993). Although much of the improvement via regulations in air quality management has been imposed by public agencies to eliminate air pollutants, including SO_x and NO_x , the air quality in southern Taiwan was still getting worse in the last decades

due to the secondary pollutant, such as ozone and particular matters, which were in excess of the regulatory standards from time to time. In particular, ozone has become the criteria pollutant of most concern in air pollution episode in southern Taiwan since 1997. Up to 2003, prevalence of adulthood asthma in southern Taiwan is 2.94%, the highest one among Taiwan (Guo et al., 2004). Public health is under the threat of serious air pollution, especially the ozone pollution. However, ground-level ozone concentration shows strong seasonal, episodic, and diurnal fluctuations. The fate of surface ozone became a critical subject for industrial pollution control strategy and health risk assessment.

Traditionally, ozone pollution was only thought to be a photochemical problem related to meteorological and diffusive process. For this purpose, models with reasonable accuracy have to consider physical and chemical relations among ozone and its relevant reactants, precursors under

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various meteorological conditions simultaneously (Stefano, 1996). However, all the above modeling efforts were tied with an uncertainty problem that can never be expressed analytically by simplified processes. One of the most important problems is the uncertainty embedded in emission identification, including biogenic source, industrial source, and relevant chemical mechanisms among ambient pollutants. No matter how good the inventory analysis was implemented in a large-scale modeling analysis, such as the integrated MM5-CAMQ modeling approach, the uncertainties in the mechanistic modeling process can be manually tuned away but never disappear in reality. Because all the meteorological and photochemical reactions involved are so complex, the synthesis of both nonlinear and linear models are still difficult to simulate it well with limited knowledge of such highly complex system. Hence, two relatively new tools in system sciences, which are chaos dynamics and fractal statistics, were used to explore the ground-level ozone time series analysis in this study.

Nonlinear dynamics and complex system analysis were first developed in the empirical framework of the nature in science, and were rapidly applied into different research fields in recent decades. Lorenz (1963) was the first person who found chaotic characteristics, i.e., Lorenz attractor, for the atmospheric system, which was the well-known “Butterfly Effect”, and started the era of chaos research. Li and Yorke (1975) then gave a definite word “chaos” to describe the behavior that seems intuitively disorder but is of deterministic rule; by their simulation, many irregular phenomena seem to obey a hidden rule in the nature. This discovery aided in many studies that employed methods and techniques via nonlinear dynamics to analyze different observed time series. Up to now, most empirical findings gave more evidence with respect to the underlying chaotic nature of the time series, which exhibit high nonlinearity. Due to such nonlinear characteristics, many assumptions in linear models are failed so that linear models might not be suitable for such nonlinear system studies (Liu and Lin, 1998; Weron and Przybyłowicz, 2000). Even more, nonlinearity implies chaos. For ground-level ozone research, more and more nonlinear time series methods became in favor of providing advanced information for the chaos dynamics, forecasting and nonlinearity analysis (Lee et al., 1994; Chen et al., 1998; Kasim et al., 2000; Windsor and Toumi, 2001).

Nonlinear statistics was first proposed by Hurst (1951) who worked for the flood control strategy in Nile River with the concept of self-affined events with memory, i.e., rescaled range (*R/S*) analysis. Those time series reveal universal power laws governing their variability with long memory. From his study, the Hurst exponent was proved to be a precise indicator estimating the scale-unchanged characteristic and be interpreted as further evidence of the universality of the law. A long-memory process analysis was later modified by Mandelbrot and Wallis (1969) and Mandelbrot (1982), Peters (1994, 1996), and was applied to many natural phenomenon studies and economic data

analysis in recent years. Excluding *R/S* analysis, some nonlinear statistic methods such as BDS test and fractal time series analysis were developed as well. Recent studies show the distinguished achievement of the nonlinear complex system analysis in fractal nature study, such as rainfall data analysis, fluid mechanics, El Niño frequency study, topography research, traffic flow system, urban growth study, economical analysis, and air pollution analysis, it can help analyze the nonlinearity of system and reconstruct the underlying characteristics, such as behavior attribute, memory effect, self-affinity, fractal dimension, nonperiodic cycle length etc., in local or regional systems (Rodriguez-Iturbe et al., 1989; Mayer, 1992; Peters, 1996; Papaioannou and Karytinos, 1995; Krugman, 1996; Caccia et al., 1997; Tuck and Hovde, 1999; Kawaku et al., 1999; Weron and Przybyłowicz, 2000; Hall et al., 2001; Ryuji and Atsushi, 2001; Zhu and Liu, 2003; Daniel and Benjamin, 2005). Persistence and long-memory effects could provide a totally different viewpoint for the analysis of extreme events, but it might not end up a short interval. Otherwise, it could really affect the system behavior much longer than we expected.

Up to now only few nonlinear characteristics of air pollution dynamics have been specified. The first nonlinear ozone dynamics study was carried out in 1994 (Li et al., 1994). They analyzed the hourly average ozone concentration data in Cincinnati city and found the ozone series was deterministic with a correlation dimension of 3 in the sampling period. But the results of their study could not specify if the ozone series was with colored noise. After that, Raga and Le Moyne (1996) analyzed hourly air pollutant data at 13 stations in Mexico City; their results from nonlinear analysis suggested ozone dynamics was not a random process and estimated the correlation dimension of the ozone series was 10 in the sampling period. Kasim et al. (2000) estimated the correlation dimension of daily average ozone series as 3, and furthermore developed a local short-term prediction model on the basis of chaos theory. Tuck and Hovde (1999) first calculated the Hurst exponent estimator of 0.57 from airborne ozone measurements; Windsor and Toumi (2001) applied *R/S* analysis, Sigma-T (ST), and kurtosis analysis to average hourly ozone, PM₁₀, and PM_{2.5} series in UK and got mean Hurst exponent estimator of 0.77, 0.80, 0.77, respectively. Their study proved the long-memory effect of ozone series with persistent duration up to 400 days. Zhu and Liu (2003) used *R/S* analysis to estimating the long-range dependence of weekly hydrogen ion deposition and the Hurst exponent estimator are with mean 0.72 and 0.52 within two different temporal scaling regimes, respectively; in addition, the persistent duration of a long-memory effect may persist 6–9 years.

When facing the crucial ozone pollution, it is important to characterize its variant behavior driven by the interaction between human activities and natural system. For exploring the volatility of ground-level ozone dynamics in southern Taiwan, this study investigates the issue more

thoroughly by applying a nonlinearity statistical analysis. In the following sections, we will introduce nonlinear fractal statistical methods and end up with a case study in two special sites selected in southern Taiwan for the purpose of demonstration.

2. Methods

2.1. Rescaled range (R/S) analysis

R/S analysis was first suggested by Hurst to account for the inherent nature of nonlinearity in a Nile River flood control project in which long records of natural phenomena was analyzed. There appeared to be cycles and long-term dependence in the river data. However, standard analysis revealed no statistically significant correlation between observations. As a result, Hurst developed a method called the rescaled range (R/S) for distinguishing completely random time series from correlated time series (Peters, 1994; Peters, 1996).

The analysis of time series is proven useful for identifying trends, nonrandom chaotic determinism, and fractal structure of the data set. In this paper we investigate it by the R/S analysis method modified by Peters (1994). The analysis begins with dividing a time series of length N into d subseries $X_a(x_1, x_2, \dots, x_n)$ of equal length n for $a = 1 \dots d$, such that N equals d multiply n . Then, for any possible subseries $n < N$, a cumulative time series could be obtained by

$$X_{i,a} = \sum_{i=1}^n (x_i - M_a) \quad \text{for } i = 1 \dots n, \quad (1)$$

where M_a is the series mean

$$M_a = \frac{1}{n} \sum_{i=1}^n x_i. \quad (2)$$

Then the range of the cumulative deviation R_n is obtained as the difference between the maximum value and minimum value of $X_{i,a}$

$$R_n = \max(X_{i,a}) - \min(X_{i,a}). \quad (3)$$

The mean value of the rescaled range for subseries X_a of length n is

$$\left(\frac{R}{S}\right)_n = \frac{1}{d} \left(\frac{R_a}{S_a}\right), \quad (4)$$

where S_a is the time series standard deviation

$$S_a = \left[\frac{1}{n} \sum_{i=1}^n (x_i - M_a)^2 \right]^{0.5}. \quad (5)$$

Hurst found that the ratio R/S analysis is very well described for a large number of natural phenomena by the following empirical relationship (i.e., a power law):

$$\left(\frac{R}{S}\right)_n = (c \times n)^H, \quad (6)$$

where c is a constant. After taking logarithmic on both sides, Eq. (6) becomes

$$\log\left(\frac{R}{S}\right)_n = \alpha + H \log(n) + \varepsilon, \quad (7)$$

where α is the regression constant term, and ε is the regression error term.

We could perform an ordinary least squares regression on $\log(n)$ via $\log(R/S)_n$. The slope of the equation is the estimator of the Hurst exponent H . It should be noticed that small value of n produce unstable estimate.

Anis and Lloyd (1976) developed the following equation to circumvent the systematic deviation of the R/S statistic for small n :

When $n < 300$

$$E[(R/S)_n] = \left[\left(\frac{n-0.5}{n} \right) \times \left(\frac{n \times \pi}{2} \right) \right]^{-0.50} \sum_{r=1}^{n-1} \sqrt{\frac{n-r}{r}}. \quad (8)$$

When $n > 300$

$$E[(R/S)_n] = \left(\frac{n \times \pi}{2} \right)^{-0.50} \sum_{r=1}^{n-1} \sqrt{\frac{n-r}{r}}. \quad (9)$$

The deviation of Hurst exponent H (i.e. the standard deviation of a Gaussian white noise) could be estimated by the following equation:

$$\text{Var}(H)_n = \frac{1}{n}. \quad (10)$$

Previous studies suggested that we may perform a data prewhiting process, or detrending to eliminate the linear dependence and the nonstationarity by using the AR(p) residual before conducting the R/S analysis. It may lead to reduce the possible estimation bias due to linear dependence. (Peters, 1994; Yun et al., 1998). Katsev and L'Heureux (2003) suggested that the Hurst exponents measured from short datasets (less than 500 points) would be usually too large for most practical purposes. Peters (1996) also suggested that R/S analysis might need datasets that contains 10 times more than its nonperiodic length to confirm the reliability. Advanced algorithms of R/S analysis were developed to promote the parameter estimating efficiency and performance (Granger and Zhuanxin, 1996; Caccia et al., 1997; Craig, 1999; Kendziorzski et al., 1999; Reisen and Lopes, 1999; Jung and Shao, 2000; Breidt and Hsu, 2002).

If the process is a random walk process, i.e., statistically independent processes without long-run statistical dependence, it should give $H = 0.5$, and future predictions of the time series are impossible. Series consisted of memory effect is called a fractional Brownian motion. Such memory makes correlation among the increments of the discrete series. The Hurst exponent of $0.5 < H < 1$ corresponds to a persistent, or trend-reinforcing behavior. Persistence means that if the curve has been increasing for a period, it is expected to continue for another period and could be regarded as a biased random walk process. And the degree

of persistence depends on the extent for H close to 1. On the other hand, a Hurst exponent of $0 < H < 0.5$ shows an anti-persistent, ergodic, or mean-reverting behavior, i.e., after a period of decreases, a period of increases tends to show up. And the degree of anti-persistent depends on the extent for H close to 0.5. System dynamical properties of various Hurst exponents are shown in Table 1.

The relation between the Hurst exponent and the fractal dimension is simply $D = 2 - H$ (Peters, 1994). That means for statistically independent fractional Brownian movement, with $D = 1.5$, the Hurst exponent should be $H = 0.5$, as said before. For the various natural phenomena with H being about 0.72, the fractal dimension D is about 1.28. Overall, the Hurst exponent (H) is a statistical measure used to classify time series. $H = 0.5$ indicates a random series while $H > 0.5$ indicates a trend reinforcing series. The larger the H value is, the stronger the persistence.

The long-memory characteristic causes the appearance of trends and cycles, i.e., Joseph effect (Peters, 1994, 1996). In chaos theory, nonperiodic cycles exist and make cycles fluctuated. Nonperiodic cycle has no absolute frequency. Instead, it has an average frequency. This cycle length is defined as the average period that the memory of series dissipates, i.e. the persistent duration period. Since the Hurst exponent denotes the behavior of the series. The nonperiodic cycle length could be discerned from the $\log(R/S)_n$ versus $\log(n)$ plot as a break point appears once the data is long enough. The break means the change of system behavior. That is just where the long-memory effect dissipates. An additional statistic conducted is the V statistic. The V statistic is defined as follows:

$$V_n = \frac{(R/S)_n}{\sqrt{n}} \quad (11)$$

It could help identify the nonperiodic cycle lengths of the time series and therefore be used as a more precise measurement of the Hurst exponent. Namely, an optimal Hurst exponent must be estimated in one cycle by regression analysis (Yun et al., 1998). Although R/S could strongly explore the intrinsic characteristic of data, it could not distinguish between fractional Gaussian noises and fractional non-Gaussian noises. Furthermore, Kawaku et al. (1999) suggested R/S analysis and the BDS test can be

used simultaneously. Empirically, the BDS test is more robust distinguishing nonlinear characteristics if the Hurst exponent is close to 0.5; in such case, nonlinearity can be firmly confirmed by the BDS test.

2.2. The BDS test

BDS test was proposed by Brock et al. (1996) and generalized by Savit and Green (1991), Wu et al. (1993), and Brock et al. (1996). Time series from natural observations usually reveal highly irregular. The BDS test is a powerful tool distinguishing independent and random series.

The BDS test is on the basis of the correlation integral concept (Grassberger et al., 1991; Apostolos and Periklis, 1997; Cees, 2003). Given a time series $\{x_t; t = 1, 2, \dots, N\}$ which is a random sample of independent and identically distributed (i.i.d.) observations, the correlation integral $C_m(\varepsilon)$ measures the probability that any two of the points $\{X_i\}$ meet within distance ε from each other in m dimension phase space and must equal to the product of the individual probabilities, provided that pairs of points are independent:

$$C_m(\varepsilon) = \prod_{i,j(i \neq j)} p(|x_i - x_j| < \varepsilon) \quad \text{for } N \rightarrow \infty. \quad (12)$$

Furthermore, if all observations are also identically distributed, then

$$C_m(\varepsilon) = [C_1(\varepsilon)]^m \quad \text{for } N \rightarrow \infty. \quad (13)$$

The statistic:

$$B(m, \varepsilon, N) = N^{0.5} [C_m(\varepsilon) - C_1(\varepsilon)] \quad (14)$$

would converge to a normal distribution with zero mean and a variance $V(m, \varepsilon, N)$ which could be consistently estimated from the sample data. Thus the BDS statistic is defined as

$$W(m, \varepsilon, N) = \frac{B(m, \varepsilon, N)}{[V(m, \varepsilon, N)]^{1/2}} \quad \text{for } N \rightarrow \infty. \quad (15)$$

The BDS statistic, W , would obey a standard normal distribution, and statistical inference is possible. The null hypothesis of BDS test is the testing series is of whiteness (i.i.d. observations). If the W estimator is larger than the level of significance, we can reject the null hypothesis, that is, the nonlinearity exists in the testing series.

It has been shown by Monte-Carlo simulations (Apostolos and Periklis, 1997) that even for quite small samples ($N = 500$), the BDS statistic could approximate i.i.d. data well enough from different common statistical distributions. And it could detect linear, stochastic nonlinear, and deterministic nonlinear departures from i.i.d.-ness, for ε values between 0.5 and 2 standard deviations of the data and m values between 2 and 6 (Papaioannou and Karytinis, 1995).

Hence, standard statistical analysis in this paper began with assuming that the system under study is primarily

Table 1
Properties of system behavior for various Hurst exponents (Peters, 1994)

H	Classification	System behavior
0	—	Random stochastic process
(0, 0.5)	Pink noise	Anti-persistent, ergodic, or mean-reverting process
0.5	White noise	Series without long-memory; system is non-predictable
(0.5, 1)	Black noise	Persistent, trend-reinforcing, or fractional brown motion, most common in nature system
1	—	Single direction linear motion

random, but such assumptions might fail to most models describing the real world. Thus the BDS test is a powerful test for distinguishing linear i.i.d. systems from deterministic chaos or nonlinear stochastic systems. But it is weak to differentiate whether or not the nonlinearity is from deterministic chaos or from nonlinear stochastic systems. For this reason, it could not be considered as an overall test for chaos. Instead, it should be regarded as a test of misspecification to be applied at the post fitting stage so that nonlinearity arisen here would be consistent with the chaotic explanation.

3. Case study

Kaohsiung metropolitan region is a highly industrialized area in southern Taiwan with a variety of centralized manufactories clustered in suburban divisions geographically. Long-term violations of air quality standards with respect to two species, namely ozone and particulates, triggering infections and allergens in this city need to be taken into account particularly. For the assessment, two neighboring sites (e.g., Chaozhou and Zenwu) in the suburban region, where tend to suffer as much or more from pollution than their downwind neighbors, were selected as candidate sites for study (see Fig. 1). Zenwu is highlighted with its high-density petrochemical industry at upwind geographical position. On the other hand, there is no obvious industrial facility in Chaozhou, but the prevailing wind brings precursors to this downwind town. If the sunlight provides enough energy, a good photochemical condition is formed. This downwind effect made Chaozhou the most polluted city of ozone in this region. Thus, the dynamic relationship between these two sites is important to explain the major air pollution dynamics in southern Taiwan.

The trend in highest “Daily Maximum 1-h Ozone Concentration” extracted from official monitoring databases that are routinely collected by the Environmental Protection Administration (EPA) in Taiwan was analyzed by a nonlinear time series scheme in this study. There are 1.13% and 1.96% scattered missing values in the original

monitoring data sets associated with Chaozhou and Zenwu in the study period, respectively, and all of them were reorganized by the interpolated data created based on their neighboring data points. Thus “Daily Maximum 1-h Ozone Concentration” for a 7-year time span (e.g. from January 1994 to December 2002) were used and the time series plots at both sites are shown in Fig. 2. The time series, however, reveal implicit seasonal trend in the data. In Fig. 2, from the time series plot, it turns out that the peak ozone concentrations are higher in winter seasons. This might be inconsistent with higher ozone peaks observed in many other locations (e.g., in summer seasons). However, it is known that ozone concentrations are the responsive outputs in a composite system with photochemical and meteorological features collectively. Thus, if the source emissions of precursors are assumed to be kept constant all the year, the meteorological factors would dominate the transport and fate of surface ozone. Given the fact that Kaohsiung is located in a tropical climate zone, and the temperature variation between winter and summer is just about 15°C, the winter season is not substantially long enough to cool down the environment. This obviously implies the photochemical process may be not the most critical factor of ozone formation in this region as long as NO_x and VOC_s emissions remain the same a year round. In contrast, throughout the seasonal change, the frontal cyclones can be classified into 53 patterns that create a differential environment for ground level ozone transport. In the summer southern Taiwan is deeply affected by typhoon and thunderstorm, while in the spring the monsoon dominates the weather system periodically. The torrential rainfall in the summer may favor the wet deposition of the some precursors creating a random episode locally. Patterns of mixing height spatial

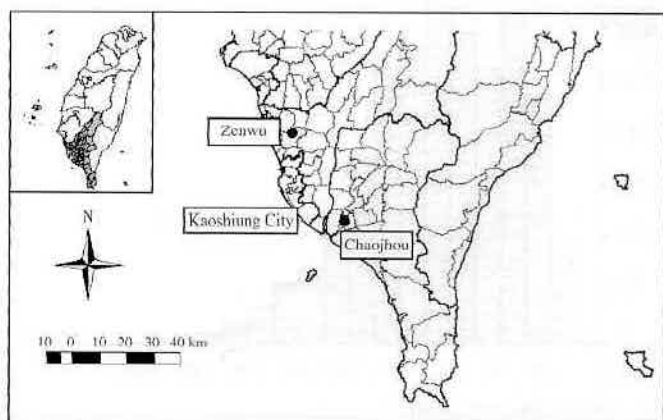


Fig. 1. Geographical location of the study area.

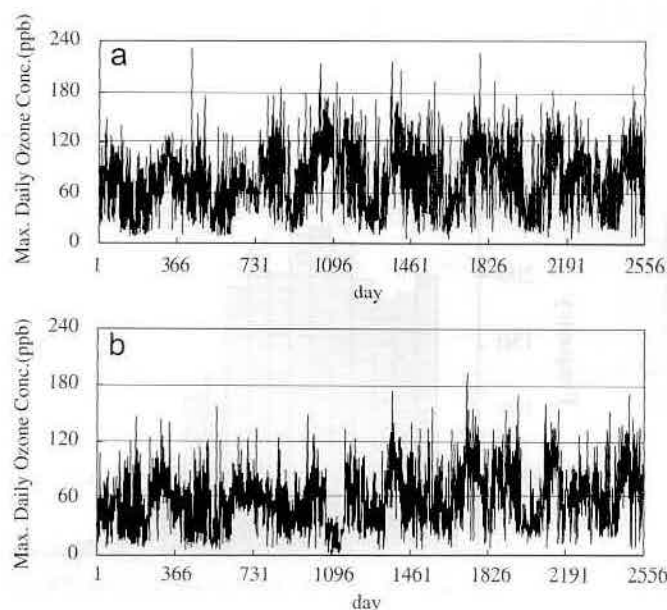


Fig. 2. Series of daily maximum hourly ozone concentration at (a) Chaozhou and (b) Zenwu monitoring sites (1994/1/1–2000/12/31).

and temporal variability in the Kaohsiung area were unique too. Boundary layer heights over land in the Kaohsiung area appeared to be somewhat lower in winter compared to in summer. As a consequence, this affected air pollutants fate and transport in the winter resulting in an inherently chaotic pattern. Thus, it is not surprising that the peak ozone concentrations are higher in winter seasons.

Furthermore, the ozone data seem very much collated with each other at the two monitoring sites except around day 1096. Considering the two sites are located in the same region, one might be curious about whether there was any particular air quality episode causing this or not. It was actually not. One reason for causing this phenomenon is that the aerial time series of peak hourly ozone concentrations were collected routinely in every day on an hourly basis so that the maximum concentrations at these two sites might appear in different time window temporally. On the top of that, these two sites play different roles in the surface ozone formation spatially. There are 40 Km distance in between these two cities. In Zenwu, there are several large-

scale petrochemical plants which constantly contribute to the ozone precursor emissions; on the other hand, Chaiojhou, where there is no any local emission of ozone precursors, presents a totally different environment of surface ozone formation where the aggregation of the photochemical reaction and short-range precursor dispersion mechanisms occurs collectively. The meteorological investigation reveals that Zenwu's weather condition is more linked with sea breeze on a daily basis locally whereas Chaiojhou is located more closed to the mountainous area so that the wind pattern could be impacted by the local circulation in complex terrain. This observation supports the occurrence of such different monitored records near the 1096 day given that there was a significantly different wind speed which was larger in Zenwu and smaller in Chaiojhou.

Table 2 presents basic statistics of the data. Although the skewness and kurtosis of both time series are close to normal distribution levels, the variance is quite irregular and large. Besides both positive kurtosis denote the series are a little fat-tailed—this is one characteristic of fractal brown motion (Peters, 1996; Windsor and Toumi, 2001). Fig. 3 shows the histogram of the data, and they are different from normal curves. In addition, the data failed in the normal distribution test using the Kolmogorov–Smirnov statistics. The autocorrelation relationships expressed as a function of the lag associated with the two ozone time series data are shown in Fig. 4, respectively; linear strong long-range interdependence obviously exists in both time series data. This is one of typical characteristics of nonlinear dynamic system (Peters, 1996). Thus further nonlinearity test has to be carried out.

The power spectrum analysis was used to evaluate the nonlinearity of the data, and the results were shown in Fig. 5. In Fig. 5(a) and (b), both long tails exist significantly to the right of the figures indicative of the strong fractality in both original time series. The following *R/S* analysis was therefore performed to seek for detail parameters. The

Table 2
Summary of statistics (daily maximum hourly ozone concentrations)

Site	Chaiojhou	Zenwu
Period covered	1/1/1994–12/31/	1/1/1994–12/31/
Sample size	2557	2557
Mean	76.16	59.10
Standard deviation	39.12	30.33
Median	74.4	56.80
Kurtosis	0.379	0.069
Skewness	−0.298	0.566
Kolmogorov–Smirnov statistics	0.045 ($p < 0.01$)	0.048 ($p < 0.01$)
Maximum	231.9	191.2
Minimum	0.9	2.3

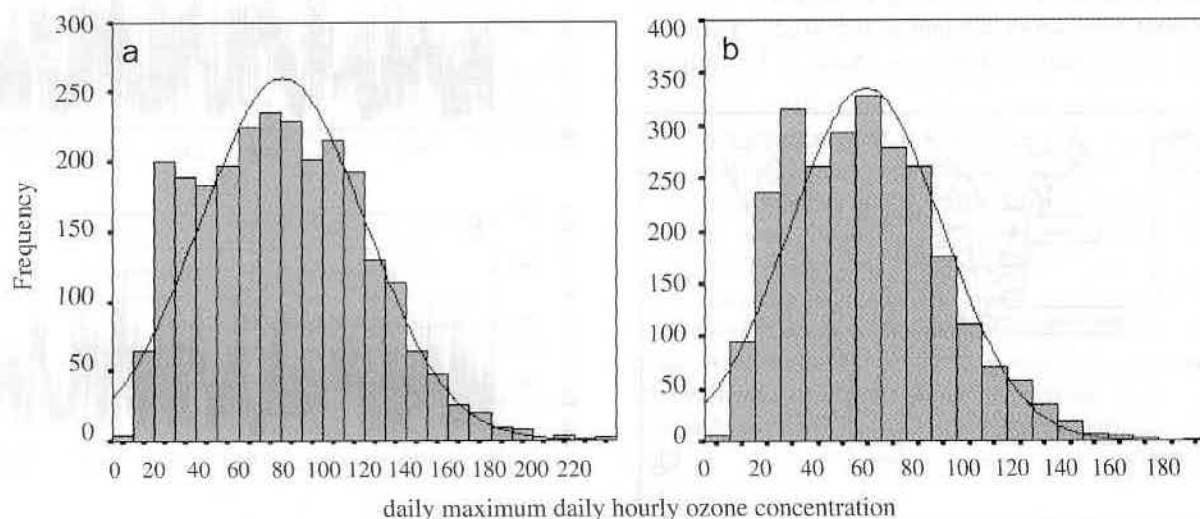


Fig. 3. Histogram plot of maximum daily ozone series at (a) Chaiojhou and (b) Zenwu.

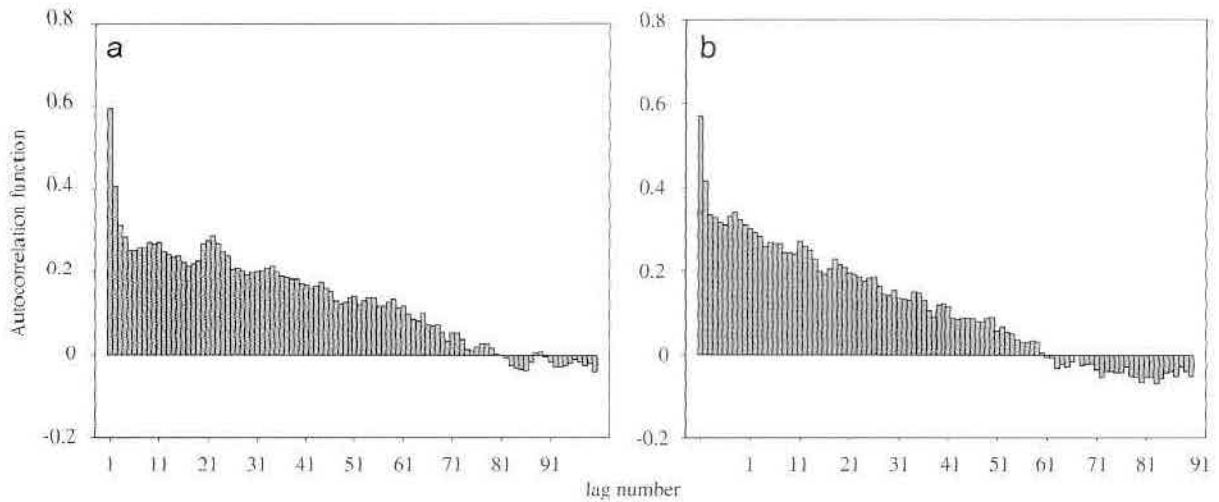


Fig. 4. Autocorrelation function plot of maximum daily ozone series at (a) Chaozhou and (b) Zenwu.

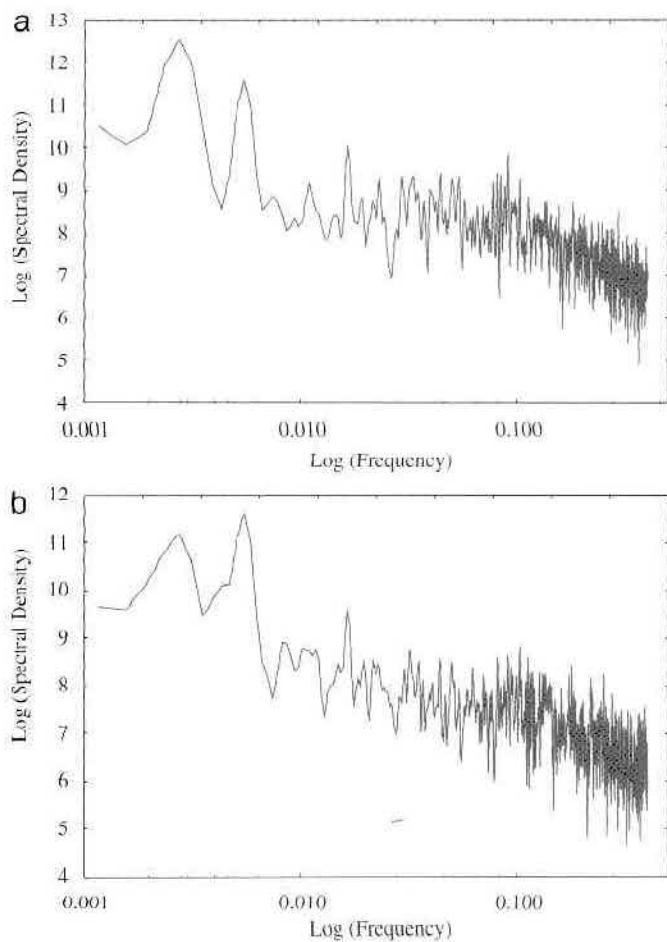


Fig. 5. Power spectrum of the maximum daily 1-h ozone concentration time series for (a) Chaozhou and (b) Zenwu stations

Hurst exponent was measured by AR(1) residuals of the original time series to reduce or at least minimize possible estimation bias due to linear dependence (Peters, 1994; Yun et al., 1998).

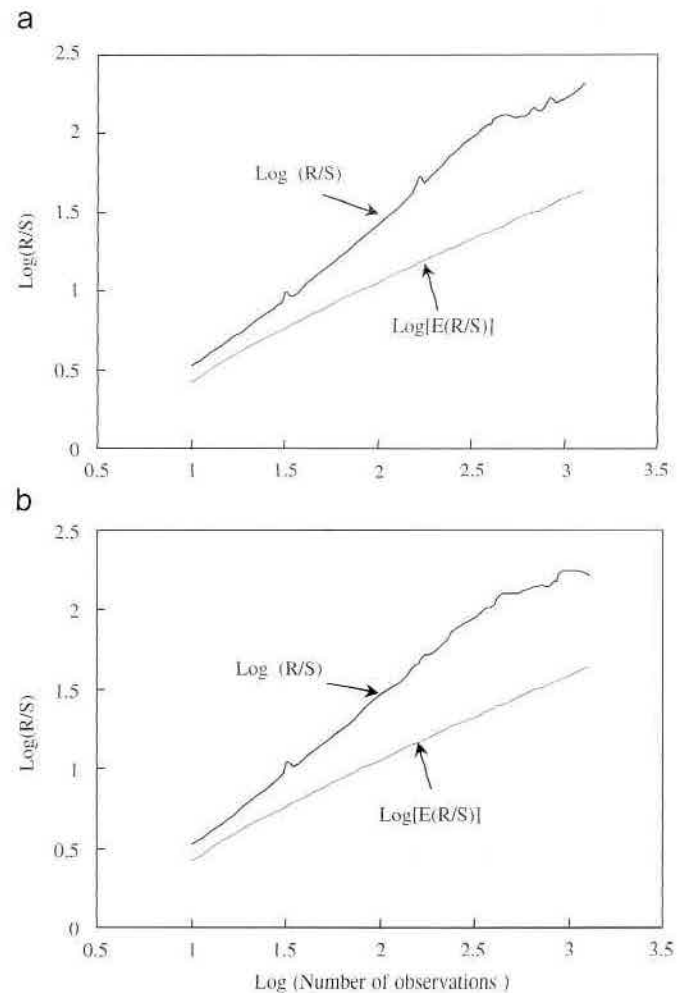


Fig. 6. R/S analysis for (a) Chaozhou and (b) Zenwu station.

Figs. 6(a) and (b) are the R/S analysis results; $E(H)$ for i.i.d. random series with $H = 0.5$ could be calculated from Eq. (9) with variance 0.039 (i.e. $1/T$). Since the estimated curves associated with both sites are different from $E(H)$

curve, we can exclude the possibility that the corresponding ozone time series are random systems. The value of H calculated for Chaozhou and Zenwu are 0.758 and 0.748, respectively. Both the values of H estimated are significantly larger than 0.5 (random walk behavior), the maximum daily 1-h ozone time data series are proved persistent with fractional Brownian motions intrinsically. The irregular fluctuations and trend could be endogenously due to several environmental factors atmospherically, such as temperature, light density, cloud cover, wind velocity and wind direction, and the spatially heterogeneous emissions of air pollutants. Even a small change of each controlling factors could result in a deep effect in these surface ozone formation and dispersion processes. Furthermore there is no obvious difference between the value of H in the downwind mixing area and zone where precursors emit, and this discovery suggests that the Kaoshiung-Pindong area could be integrated as a regional ozone system and is governed by a long-memory effect. Since the H estimated at Chaozhou is larger than that at Zenwu, this implies a longer memory effect is phenomenal at Chaozhou located downwind of those emission sources in this area.

Figs. 7(a) and (b) are V statistic plots of the two interested sites. The two plots almost show similar “break-points,” where the nonperiodic cycle occurs. The break appears exactly at 32, 170, and 420 days, simultaneously. Nonperiodic cycle length of 32 day was intuitively identical to the period by month as a short behavior cycle. That might denote the lag period of short memory of specific routine but unknown events. Cycle length of 170 day could be viewed as meteorologically seasonal factor proved by previous studies in this area, which show that high-pressure air parcel was formed in this area from the end of fall to spring because of the leeward shore effect and made the mixing height lower favoring the photochemical reaction (Cheng, 2001; Chen et al., 2003). Cycle length of 420 day is consistent to the 416 day—the result from UK ozone data (Windsor and Toumi, 2001). Given that there was no clue with regard to the regional meteorological patterns, the 420-day nonperiodic cycle might imply some sort of intrinsic atmospheric pattern temporally with much longer scale. Besides, Windsor and Toumi (2001) also indicated that the complexity of ocean-atmosphere system favors higher Hurst exponent; of course the system in southern Taiwan falls into the same category as well. These nonperiodic cycle lengths implies the lasting period of some memory-effect due to atmospheric environmental system. In terms of environmental management, ozone pollution prevention and control measures should be made based on both short- and long-term phenomena and, different types of measures should be imposed in each stage.

Furthermore, the BDS test would be required to confirm the nonlinearity of the ozone time series data. Table 3 addresses the results of BDS analysis of the time series associated with both sites with Dataplore[®] software 2.2-2 Version (<http://www.ixellence.com>). The null hypothesis of

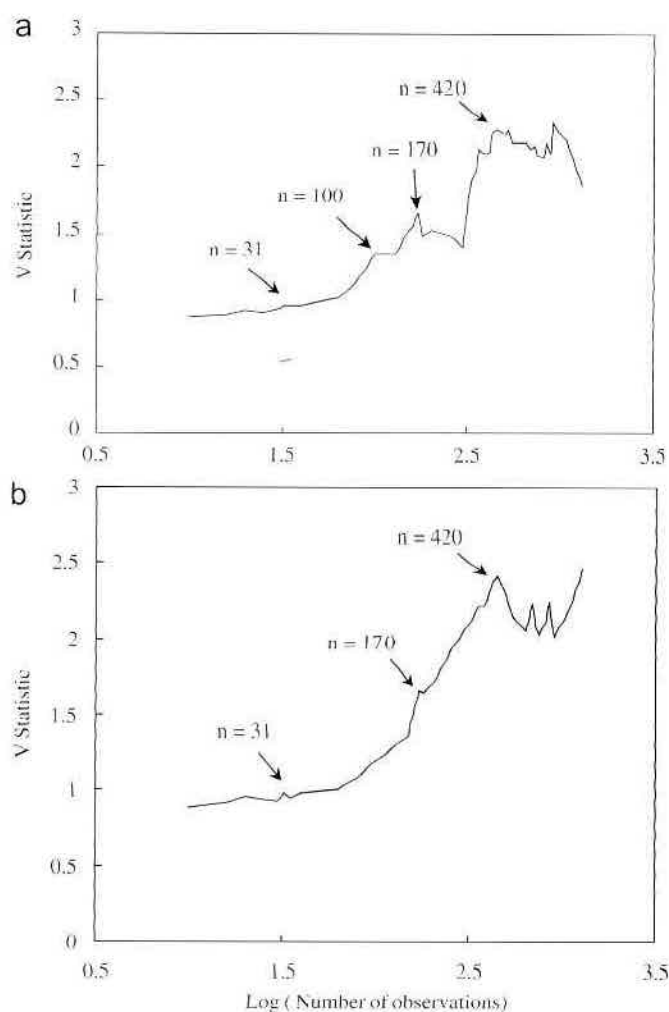


Fig. 7. V statistic plot of (a) Chaozhou and (b) Zenwu station.

i.i.d. random series will be rejected whenever $W > 1.96$ at the 5% confidence level and $W > 1.96$ at 1% confidence level. All the W values in Table 3 are significantly larger than the confidence-level values, confirming that highly nonlinearities exist in both the AR(1) residual series and original time series data. Yet the later one exhibits much higher nonlinearity than the former one. This suggests that some irregular noise may be removed by the prewhitening process, and confirms again that the intrinsically nonlinear characteristic of ozone time series does exist. This is consistent with previous analyses illuminating that the complex system behavior does affect the variations and fluctuations of ground level ozone concentrations.

4. Conclusion

When facing the needs to analyze the complex natural systems, such as air pollution due to ozone and flood impact due to unexpected storms, fractal time series analysis shows a great potential for exploring the underlying intrinsic structure of nonlinearity in nature. The Hurst exponents estimated for ground-level peak ozone concentrations are 0.748 and 0.758 at Zenwu and

Table 3
BDS statistics for maximum surface daily ozone concentration

Embedding dimension (<i>m</i>)	Chaozhou site		Zenwu site	
	Relative radius (0.05)		Relative radius (0.05)	
	Non-filtered data	Filtered data	Non-filtered data	Filtered data
2	172.29	14.59	122.65	14.74
3	235.95	20.20	149.21	20.19
4	350.68	28.85	251.89	29.59
5	557.71	41.13	388.93	42.76
6	860.53	57.72	737.33	68.39
7	1335.84	72.47	1682.56	111.09
8	1807.39	75.76	4351.62	202.84
9	1407.58	86.59	13448.67	444.21
10	—	156.49	49815.7	1163.89

Note: *W* is 2.576 at 1% confidence level.

Chowchu, respectively. It implies the maximum daily 1-h ozone time series data is a self-affine and persistent process with a long memory. Such a memory effect, however, disappears in the end of nonperiodic cycle, which is the persistence duration period. It proves that the ozone time series data are persistent with fractional Brownian motions intrinsically as well. The irregular fluctuations caused endogenously by atmospheric environmental factors may result in such a trend. The *V* statistics calculated for two towns indicate that nonperiodic cycle lengths are apparent at the cycles of 32, 170, and 420 day simultaneously. It reveals a regional-scale ozone behavioral trend, which is deemed critical in environmental management. Both the Hurst exponents and nonperiodic cycle length results from the two motoring sites are also close to the results from UK ozone series data (Windsor and Toumi, 2001). The BDS test also confirms the nonlinear characteristics of ground-level peak ozone concentration time series.

Overall, the main findings suggest that strong persistence and long-memory effects exist in ground-level ozone time series in urban region. The Hurst *R/S* analysis and BDS test have successfully identified the nonlinear characteristics and provide evidences for nonlinearity and fractality. Thus it is necessary to consider the possibility of deterministic chaos in dealing with the ground-level ozone management. Since *R/S* analysis is extremely robust with respect to noise, Hurst exponent can be used as a noise index when preparing simulated data. These properties make *R/S* analysis useful for studying chaotic environmental data. Persistence and long-memory effects could provide a totally different viewpoint for the implication of extreme event, however. It shows the peaks might not appear due to a short-term impact, and might be far more due to the endogenous driving forces of atmospheric system than the precursor impact. In totality, the long-memory effect really affects the system much stronger than we expected. Hence, the fractal and chaotic characteristics of the system should be taken into consideration. The sensitivity to the initial condition in a chaotic system

resulted in some unique observations in this nonlinear time series analysis, which might not be gained by using the first-principle, emission based photochemical modeling for tropospheric ozone. Besides, the study fully supports that such a nonlinear relationship should be addressed and emphasized in all surface ozone simulation and forecasting techniques. In terms of environmental management, ozone pollution prevention and control measures should be made based on both short- and long-term phenomena and different types of measures should be imposed in each stage. Finally, the paper demonstrate the pioneering study of nonlinear ozone dynamics in southern Taiwan and the parameters being verified can aid in photochemical model builders for advanced fate and transport mechanistic studies of ozone pollution. It may also lead to help the local government agencies to design appropriate ozone pollution countermeasures according to the scaling invariant characteristics. The construction of a dynamic forecasting model reflecting these elements of concerns will be the future research work.

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Coliforms removal in full-scale activated sludge plants in India

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Abstract

This paper investigates the removal of coliforms in full-scale activated sludge plants (ASP) operating in northern regions of India. Log 2.2 and log 2.4 removal were observed for total coliforms (TC) and fecal coliforms (FC), respectively. However, the effluent still contained a significant number of TC and FC which was greater than the permissible limit for unrestricted irrigation as prescribed by WHO. The observations also suggest that extended aeration (EA) process operating under high mixed liquor suspended solids (MLSS) and sludge retention time (SRT) is more efficient in the removal of coliforms. Further attempts have been made to establish the relationship between two key wastewater parameters, i.e. biochemical oxygen demand (BOD) and suspended solids (SS) with respect to fecal and TC. The relationships were observed to be linear with a good coefficient of correlation. The interrelationship of BOD and SS with coliforms manifest that improvement of the microbiological quality of wastewater could be linked with the removal of SS. Therefore, SS can serve as a regulatory tool in lieu of an explicit coliforms standard.

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Keywords: Activated sludge process; Biochemical oxygen demand (BOD); Fecal coliforms; Suspended solids (SS); Total coliforms

1. Introduction

In the Indian subcontinent, raw or treated wastewater is reused for various purposes without proper microbiological quality assessment. A large population of the country still uses water directly from surface water bodies for drinking and other contact uses without appropriate treatment, thus exposed to water borne diseases. This is the single major cause of nearly 80% of human mortality in India. Children are the worst affected, especially in rural areas and urban slums (CPCB, 2002–2003). The potential presence of pathogens in polluted water is assessed using indirect measures such as coliform bacteria, which indicates the safety of water. WHO (2002) has recognized coliforms (total coliforms (TC) and fecal coliforms (FC)) as the key fecal indicator. These indicators provide a total spectrum of water borne diseases, viz. TC to indicate the

presence of bacterial pathogens while FC indicates the presence of bacterial pathogens as well as the presence of enteric viruses through their relationship being with coliphages (APHA, AWWA, WEF, 1998).

Thus, the effectiveness of wastewater treatment systems with respect to the elimination of microbiological pollution is often measured by determining the densities of TC and FC in effluent of wastewater treatment plants. An extensive review of the published data indicates that activated sludge process is an effective treatment system for microbiological removal from wastewater. The overall efficiency of coliforms removal has been reported to be 90–95% and 90–98% in complete mix and extended aeration (EA) activated sludge processes, respectively (Arceivala, 2004). James (1985) reported 97% coliforms removal by conventional activated sludge system. Earlier studies on activated sludge plants (ASP) have shown similar 90–99% enteric bacterial reductions (Koivunen et al., 2003).

Consequently, there is a need to evaluate and to improve the treatment efficiency of existing wastewater treatment facilities in terms of microbial removal. The performance

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of sewage treatment plants is assessed by monitoring of indicator bacteria (TC and FC) in grab samples of the effluent. In addition, the monitoring of indicator organisms, biochemical oxygen demand (BOD) and suspended solids (SS) are also used as indirect measures of the potential presence of microorganisms. Various other studies show that coliforms concentration could be more strongly correlated with BOD than SS (Williams et al., 1995). Feeham et al. (1981) reported that primary sedimentation tank, with retention time of 2–6 h, produced quite variable results in the removal of bacterial indicators. Removal is caused by the settlement of bacteria, which are adsorbed on or entrapped within SS. While many plants are capable of meeting numerical limits for BOD and SS, limited information is available on the effectiveness of full-scale systems for removal or inactivation of pathogens.

This particular study is conducted to examine as to what extent microbial indicators and pathogens are removed/inactivated through biological treatment. Another objective was to identify the key wastewater constituents that influence the removal of indicators through biological treatment systems. The relationship between key wastewater constituents, e.g., BOD and SS and coliforms could be very useful in routine monitoring and upgradation of efficiency of Sewage Treatment Plants (STPs) and also in development of microbial quality standards for activated sludge process and other modes of sewage treatment.

2. Material and methods

2.1. Sampling and sewage characterization

The type and location of sampled STPs are summarized in Table 1. In different STPs, raw and treated wastewater are collected for physico-chemical as well as microbiological analysis. Grab sampling procedure was adopted for microbiological analysis and composite sampling for physico-chemical analysis as per the methods prescribed in Standard Methods (APHA, AWWA, WEF, 1998). Wastewater samples for microbiological examination and BOD determination were collected from inlet and outlet units of treatment plants in non-reactive sterilized borosilicate glass bottles of 250 ml capacity each. The samples were transported in ice to the laboratory. The samples taken from ASP Haridwar were analyzed in Environmental Engineering Laboratory of Civil Engineering Department, IIT Roorkee and the samples collected from ASPs, Delhi were analyzed in the Water and Wastewater Laboratory at Central Pollution Control Board (CPCB), Delhi. The samples were analyzed on the same day of sample collection.

2.2. Sample analysis

TC and FC were enumerated by multiple tube fermentation technique as described in Standard Methods for the examination of water and wastewater, by using Lauryl

Table 1
Descriptive data and removal efficiency of activated sludge process plants in India

S. no	Location	Capacity/flow (MLD)	BOD (mg/l)			Suspended solids (mg/l)			TC (in log)			FC (in log)		
			I	E	%	I	E	%	I	E	R	I	E	R
(A) Haridwar: conventional activated sludge plant (ASP)														
1	Kankhal ^a	18/21	135	10.1	92.52	299	14.4	95.1	7.5	5.1	2.4	7.3	4.8	2.5
(B) Delhi: conventional activated sludge plants (ASP)														
2	Nilothi	182/15	90	4	95.6	432	21	95.1	7.8	5.1	2.7	7.7	4.8	2.9
3	Cor.Pillar-I	45/64	48	15	68.8	342	93	72.8	7.9	5.8	2.1	7.6	5.3	2.3
4	Cor.PillarII	91/57	48	15	68.8	342	93	72.8	7.9	5.8	2.1	7.6	5.3	2.3
5	Keshopur	182/106	282	10	90.2	404	21	94.8	8.1	6.7	1.9	8.6	7.1	1.5
6	Okhla-I	73/41	207	48	76.8	291	83	71.5	7.7	6.0	1.7	7.4	5.7	1.7
7	Okhla-II	168/159	249	12	95.2	480	32	93.3	8.3	6.1	2.2	8.0	5.9	2.1
8	Okhla	205/182	249	19	92.4	480	27	94.4	8.3	6.6	1.7	8.0	5.8	2.2
9	Yamuna Vihar I	45/27	174	17	90.2	391	44	88.8	9.1	7.3	1.8	8.6	6.7	1.9
10	Yamuna Vihar II	45/15	199	20	90	405	39	90.4	9.2	6.9	2.3	8.6	6.7	1.9
11	Najafgarh	23/2	54	1	98.2	165	29	82.4	7.0	5.5	1.5	6.7	5.1	1.6
12	Papankalan	91/38	103	10	90.3	142	39	72.5	7.1	5.1	2.0	7.0	4.8	2.2
13	Kondli Phase I	45/57	241	27	88.8	363	68	81.3	8.8	7.4	1.4	8.5	7.1	1.4
14	Kondli Phase II	114/58	261	34	87	604	45	92.6	9.0	6.7	2.3	8.7	6.3	2.4
15	Kondli Phase III	45/28	237	14	94.1	519	16	96.9	8.8	6.4	2.4	8.6	5.1	3.5
16	Rithala Old	182/46	205	14	93.2	330	75	77.3	9.0	7.5	2.5	8.9	6.7	2.2
17	Narela	45/3	100	8	92.0	426	38	91.1	7.2	5.0	2.2	7.0	4.6	2.4
(C) Delhi: extended aeration plants (EA)														
18	Mehrauli	23/5	126	7	94.4	251	12	95.2	8.5	5.7	2.8	8.3	4.3	4.0
19	Vasant Kunj ^b	14/8	250	23	91	410	80	80	7.7	4.6	3.1	7.5	4.3	3.2

I = influent, E = effluent, % = percentage removal, R = log removal.

^aAverage data of one year study (April 2004–March 2005).

^bAverage data of one year study (August 2005–July 2006).

Tryptose Broth incubated at $35 \pm 1^\circ\text{C}$ (24–48 h) for TC and EC-medium incubated at $44 \pm 1^\circ\text{C}$ (24–48 h) for FC (APHA, AWWA, WEF, 1998). BOD was defined as the amount of oxygen consumed in the sample over 5 days at 20°C , according to Standard Methods (APHA, AWWA, WEF, 1998) and data were expressed in mg of O_2/l . SS were estimated as the weight of solids material retained on a pre-weighted Whatman filter paper after filtering a known volume of sample and drying the filter/membrane at 105°C until a constant weight was reached and data were expressed in mg/l.

3. Results and discussion

3.1. Coliform removal efficiency of activated sludge process systems

The wastewater samples collected from the inlet and outlet of ASP, Haridwar and Vasant Kunj Extended aeration plant, Delhi were analyzed for monthly/seasonal variations from (April 2004–March 2005) and (August 2005–July 2006), respectively. Inlet and outlet samples for other activated sludge plants operating in Delhi were collected and analyzed during the months of November–December 2004. Currently, all plants except two are operating under conventional activated sludge mode. The two plants operating under EA modes are Vasant Kunj and Mehrauli. Disinfection is not applied in any of the plants. Table 1 gives the descriptive data on BOD, SS and coliforms concentration in the influent and effluent of treatment plants as well as their removal efficiency.

The influent concentration of TC and FC were found to be varying between log 7–9 and 6.7–8.9 per 100 ml, respectively. In the treated effluent TC and FC values were encountered in the range of log 4.2–7.5 and 3.9–7.1 per 100 ml, respectively. The overall average removal of TC and FC by activated sludge process systems were found to be log 2.2 (99.4%) and 2.4 (99.6%), respectively. As per Metcalf and Eddy (2003), reduction of bacteria in ASP is 90–98%. Earlier studies in activated sludge plants have usually shown similar 90–99% enteric bacterial reduction (Koivunen et al., 2003).

Among all plants, comparatively higher TC and FC removal were observed in Vasant Kunj (log 3.1 and 3.2) and Mehrauli (log 2.8 and 4) EA STPs. The results are in coherence with the findings of WERF (2004) that higher levels of mixed liquor suspended solids (MLSS) and longer sludge retention time (SRT) tends to result in enhanced removal of microbial indicators and pathogens. Furthermore, in some plants (Keshopur, Okhla-I, Najafgarh and Kondli) poor SS removal in sedimentation and secondary treatment and higher coliforms concentrations in the effluent were observed.

It was observed that finally treated effluent still contained significant number of TC (log 5.8 or 2.1×10^5 MPN/100 ml) and FC (log 5.3 or 2.0×10^5 MPN/100 ml). These concentrations are greater than the permis-

sible limit (i.e. log 3 or 1000 MPN/100 ml) specified by WHO (1989) for unrestricted irrigation. It indicates that a considerable number of microbes were free in the water and could not be removed significantly by activated sludge process. Therefore, an additional treatment step is required to remove microorganisms more effectively.

In order to determine whether the observed differences between two sets of experimental data were significantly different, data were subjected to paired two sample mean *t*-test, using MS Excel. Results are summarized in Table 2. Results from paired *t*-test between BOD and TC indicate that the critical value of *t* (2.00) obtained from *t* distribution table at 5% probability level is lower than observed value of *t*-stat (6.65). Almost similar results were found between BOD and FC (Table 2) and hence null hypothesis is rejected. Thus, it can be concluded that real and significant differences exist between the obtained experimental data for BOD and TC, FC in sewage samples.

Similar paired *t*-tests conducted between SS and TC, FC indicates that the critical value of *t* obtained from *t* distribution table at 5% probability level is lower than observed *t* statistic value (Table 3). Even in this case, null hypothesis is rejected and it is concluded that the difference between the two sets of experimental data is true (not by chance) and the effect of SS on TC and FC in the sewage samples is significant. It is to be noted that the highest correlation coefficient (0.74) and the maximum difference between the *t* statistics and *t* critical values (5.73 and 5.78) were obtained for the SS and TC, FC data set. Therefore, it can be quoted that SS can be used as surrogate parameter in lieu of TC and FC for monitoring sewage treatment plant efficiency.

Another interesting observation was the nullification of seasonal effect in coliforms removal. Data observations for Haridwar ASP and Vasant Kunj Extended Aeration Plant, Delhi shows no significant variation in coliforms concentration (TC as well as FC) during all the seasons of the year.

Table 2
Results of paired *t*-test: two samples for means between BOD and TC, FC

Data pair	TC	FC
<i>r</i>	0.847	0.845
<i>r</i> ²	0.72	0.72
<i>t</i> -statistic	6.65	6.68
<i>t</i> -critical	2.00	2.00
<i>p</i>	<0.05	<0.05

Table 3
Results of paired *t*-test: two samples for means between SS and TC, FC

Data pair	TC	FC
<i>r</i>	0.83	0.86
<i>r</i> ²	0.72	0.75
<i>t</i> -statistic	7.77	7.79
<i>t</i> -critical	2.04	2.01
<i>p</i>	<0.05	<0.05

3.2. Interrelationship between coliforms (TC and FC), BOD and SS

Different researchers tried to correlate coliforms number with the concentration of wastewater constituents such as BOD, SS, etc. Williams et al. (1995) showed that coliform concentration can be more strongly correlated to BOD than SS while Fecham et al. (1981) highlighted the importance of SS. Koivunen et al. (2003) concluded that improvement of microbiological quality of wastewater could be linked to the removal of BOD and SS.

On the basis of data obtained, we tried to establish relationship between two key wastewater constituents, i.e. BOD and SS with TC and FC, by the regression analysis. From the plots of Figs. 1–4 following relationships were obtained between key parameters:

$$TC = 0.0139BOD + 5.6653 \quad (r^2 = 0.7191), \quad (1)$$

$$FC = 0.014BOD + 5.3491 \quad (r^2 = 0.7177), \quad (2)$$

$$TC = 0.0065SS + 5.6142 \quad (r^2 = 0.7204), \quad (3)$$

$$FC = 0.007SS + 5.2028 \quad (r^2 = 0.753), \quad (4)$$

All the coefficient of correlation values (r^2) were found to be varying between 0.71 and 0.75 at $p = 0.05$. The high positive values of r^2 shows a strong correlation of BOD and SS and TC and FC. The value of r^2 in all cases (0.70–0.75)

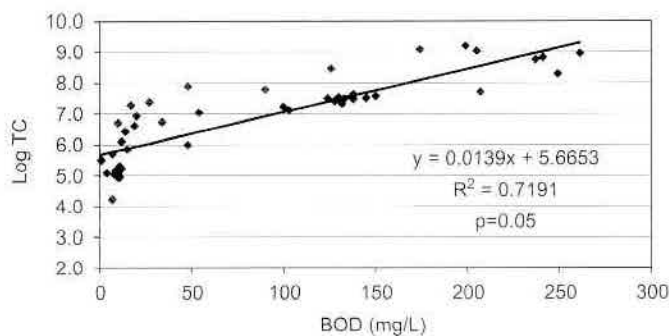


Fig. 1. Interrelationship between total coliforms and biochemical oxygen demand.

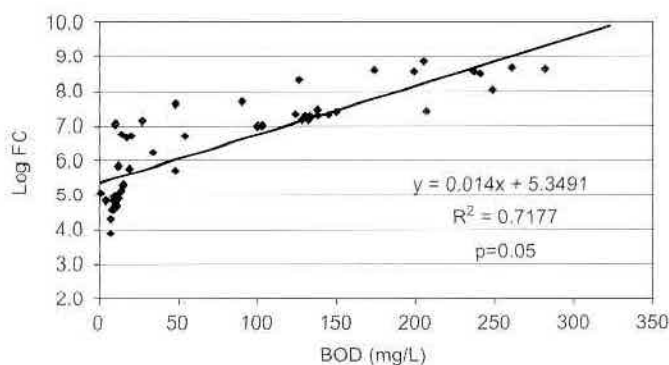


Fig. 2. Interrelationship between fecal coliforms and biochemical oxygen demand.

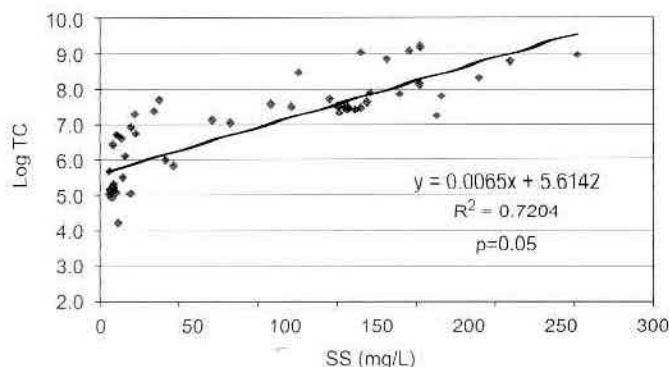


Fig. 3. Interrelationship between total coliforms and suspended solids.

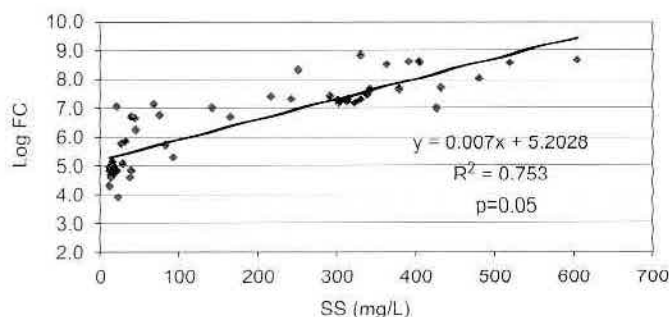


Fig. 4. Interrelationship between fecal coliforms and suspended solids.

shows that 70–75% variation in TC or FC is influenced by changes in BOD or SS concentration. However, the remaining 25–30% variations can be attributed to other factors. These interrelationships can be helpful in routine monitoring of STPs, upgradation of STP efficiency and development of microbial quality standards for activated sludge process and other modes of sewage treatment.

In order to test the significance of t -values, t distribution was employed in all four cases of data. At 5% probability level it was observed that the values of t -stat is higher than the t critical values (obtained from t distribution table) in all cases. It shows that there are less than 5% chances of error in drawing out the conclusion.

As suggested by Fecham et al. (1981), removal of bacterial indicators is affected by the settlement of SS as they are adsorbed on or entrapped within SS. The role of SS is attributed to the concentration of enteric microorganisms in the sludge flocs in activated sludge process system. Drift et al. (1977) reported that the bacterial removal could be achieved by absorption of bacteria to the sludge flocs. Thus an efficient final clarification step, which eliminates SS in wastewater, plays a key role in microbial reduction in conventional wastewater treatment system.

Therefore, for the upgradation of sewage treatment plant in terms of microbial quality, the effluent SS should be as low as possible by providing optimal treatment and settling conditions to the aeration and sedimentation tanks.

Moreover, our results implies that the microbial pollution in receiving natural waters does not solely depends upon

influent water quality, temperature or seasonal variations, rather, it is related to the efficiency of treatment process in removing organic load, i.e. BOD and SS. However, there are many process variables such as hydraulic retention time (HRT), SRT, MLSS, oxygen uptake rates (OUR) that influence the coliform removal. WERF (2004) study concludes that operation of biological treatment with higher level of MLSS and longer MCRT tend to result in enhanced removal of microbial pathogens. Finally, the authors believe that more discussion should be undertaken regarding the efficacy of process requirements with respect to microbial quality goal of secondary treated water.

4. Conclusion

Although an overall reduction of TC and FC (log 2.2 and 2.4) in ASP system has been found to be significant, yet the TC (log 5.8) and FC concentration (log 5.3) in the treated effluent exceeds log 3 or 1000 MPN/100 ml, making it unfit even for unrestricted irrigation. Interrelationship between BOD, SS with coliforms suggests that improvement of the microbiological quality of wastewater could be linked with the removal of SS. SS can serve as a regulatory tool in lieu of an explicit coliforms standard. Observations also suggest that EA process operating under high MLSS and SRT are better in the removal of coliforms. Integration of microbial seasonal monitoring with process control factors, i.e. HRT, SRT, MLSS, OUR and key wastewater parameters (BOD, SS, temperature, pH, etc.) may lead to more robust approach for assuring better microbiological quality of the treated water.

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The removal of lignin and phenol from paper mill effluents by electrocoagulation

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Abstract

This study aims to investigate the treatment of paper mill effluents using electrocoagulation. Removal of lignin, phenol, chemical oxygen demand (COD) and biological oxygen demand (BOD) from paper mill effluents was investigated at various current intensities by using different electrodes (Al and Fe) and at various electrolysis times (1.0, 2.5, 5.0 and 7.5 min). It was observed that the experiments carried out at 12 V, an electrolysis time of 2 min and a current intensity of 77.13 mA were sufficient for the removal of these pollutants with each electrode. The removal capacities of the process using an Al electrode were 80% of lignin, 98% of phenol, 70% of BOD, and 75% of COD after 7.5 min. Using an Fe electrode the removal capacities were 92%, 93%, 80% and 55%, respectively. In addition, it was found that removal of lignin, phenol, BOD and COD increased with increasing current intensity. In the experiments carried out at different current intensities, higher removal can be explained through a decrease in intra-resistance of solution and consequently an increase at the transfer speed of organic species to electrodes. It was also found that Al electrode performs higher efficiency than Fe electrode except for COD removal. However, the time required for removal of BOD was more than that of COD. The results suggest that electrocoagulation could be considered as an effective alternative to paper mill effluents treatment.

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Keywords: Paper mill effluents; Electrocoagulation; Phenol; Lignin; BOD; COD

1. Introduction

Urban industrial activity has long been identified as a major source of contaminants for aquatic environments, via atmospheric deposition and wastewater discharge. The pulp and paper industry is the sixth largest polluter discharging a variety of gaseous, liquid and solid wastes into the environment. Effluent from kraft pulping is highly polluted (USEPA, 1998).

The alkaline extraction stage of a bleach plant is the major source of colour, mainly due to lignin and derivatives of lignin. Lignin wastewater is discharged from the pulping, bleaching and chemical recovery sections. Lignin is a heterogeneous three-dimensional polymer,

composed of oxyphenylpropanoid units. It should be noted that the contamination of drinking water by phenolics at even a concentration of 1 mg/L could bring about significant taste and odour problems making it unfit for use. These effluents cause considerable damage to the receiving waters if discharged untreated since they have high levels of biological oxygen demand (BOD), chemical oxygen demand (COD), chlorinated compounds (measured as AOX), suspended solids (mainly fibres), fatty acids, tannins, resin acids, lignin and its derivatives, sulphur and sulphur compounds, etc. (Ali and Sreekrishnan, 2001; Thakur, 2004; Aksu and Gönen, 2004).

Traditional methods for dealing with the wastewater consist of biological, physical, and chemical processes and various combinations of these (Gürses et al., 2004). The typical treatment processes for pulp and paper effluents are chemical precipitation, lagooning, activated sludge and

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anaerobic treatment (Tezel et al., 2001). Recently, several physical and chemical processes for colour removal in paper mill effluents have been extensively studied, including rapid filtration through soil, ultrafiltration, ion-exchange chromatography, lime precipitation, modified bleaching sequences such as peroxide addition during extraction and the replacement of chlorine by hypochlorite, and sorption on hypo- and alum-sludge, activated carbon and allophonic compounds (Ali and Sreekrishnan, 2001). However, the problem remains unsolved, since lignin undergoes a spatial rather than chemical change and thus persists albeit in a different form, even after treatment.

Electrochemical methods are frequently used for treating wastewater which contains organic and inorganic compounds. The application of electrochemical methods to the removal of organic pollutants has some advantages compared with chemical or biological methods. Chemical oxidation methods can be used for the oxidative decomposition of many organic pollutants but these methods require large amounts of reactive chemical reagents. Biological and electrochemical methods have little or no harmful effects on the environment, because these techniques do not involve the use of harmful reagents. On the other hand, electrochemical reactions are more or less independent of the condition of the wastewater and can proceed as long as a current is supplied to the electrode (Kuramitz et al., 2001). Electrochemical technologies have attracted a great deal of attention because of their versatility, which makes the treatment of liquids, gases and solids possible, and their environmental compatibility. In electrochemical methods, the main reagent is the electron, which is a “clean reagent”. The mechanisms of the reactions that happen in electrochemical units have been studied well enough. Some chemical reactions, which occur on electrodes and in the bulk wastewater, are shown in Table 1 (Inan et al., 2004). Researchers have investigated several applications of electrochemical methods such as electrochemical treatment of wastewater containing polyaromatic organic pollutants (Panizza et al., 2000).

Electrocoagulation is a process consisting of creating a floc of metallic hydroxides within the effluent to be cleaned, by electrodisolution of soluble anodes. Compared with traditional flocculation and coagulation, electrocoagulation has, in theory, the advantage of removing the smallest colloidal particles; the smallest charged particles have a greater probability of being coagulated because of the electric field that sets them in motion. It has also the advantage of producing a relatively low amount of sludge (Pouet and Grasmick, 1995). The characteristics of electrocoagulation are simple equipment and easy operation, brief reactive retention period, decreased or negligible equipment for adding chemicals and decreased amount of sludge (Gürses et al., 2002).

Therefore, electrocoagulation has been widely used to treat water containing food and protein wastes, oil wastes, synthetic detergent, effluent mine wastes and heavy metal-containing solutions. In recent years, electrocoagulation

Table 1
Reactions at the electrodes and in the bulk wastewater

Anode	Cathode
$4\text{OH}^- + 4\text{e}^- = 2\text{H}_2\text{O} + \text{O}_{2(\text{g})}$	$2\text{H}_3\text{O}^+ + 2\text{e}^- = \text{H}_{2(\text{g})} + 2\text{H}_2\text{O}$ (in acid solutions)
$2\text{H}_2\text{O} + 4\text{e}^- = \text{O}_{2(\text{g})} + 4\text{H}^+$	$2\text{H}_2\text{O} + 2\text{e}^- = \text{H}_{2(\text{g})} + 2\text{OH}^-$ (in alkaline solutions)
$2\text{Cl}^- + 2\text{e}^- = \text{Cl}_{2(\text{g})}$	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^-$
	$\text{Cl}_{2(\text{g})} + \text{H}_2\text{O} = \text{HOCl} + \text{H}^+ + \text{Cl}^-$
<i>Al-anode</i>	
$\text{Al}_{(\text{s})} + 3\text{e}^- = \text{Al}_{(\text{aq})}^{3+}$	$\text{Al}_{(\text{s})} + 4\text{OH}^- = [\text{Al}(\text{OH})_4]^- + 3\text{e}^-$ (at very high pH)
	$\text{Al}_{(\text{aq})}^{3+} + 3\text{H}_2\text{O} = \text{Al}(\text{OH})_3 + 3\text{H}^+$
<i>Fe-anode</i>	
$\text{Fe}_{(\text{s})} + 2\text{e}^- = \text{Fe}_{(\text{aq})}^{2+}$	$\text{Fe}_{(\text{aq})}^{2+} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2 + 2\text{H}^+$
$\text{Fe}(\text{OH})_3 + \text{OH}^- = [\text{Fe}(\text{OH})_4]^-$	
$\text{Fe}(\text{OH})_2 + \text{HOCl} = \text{Fe}(\text{OH})_3 + \text{Cl}^-$	$[\text{Fe}(\text{OH})_4]^- + 2\text{OH}^- = [\text{Fe}(\text{OH})_6]^{3-}$ (at very high pH)
$\text{Fe}^{2+} + \text{e}^- = \text{Fe}^{3+}$	
$\text{Fe}^{3+} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + 3\text{H}^+$	

has been successfully used to treat various industrial wastewaters (Do and Chen, 1994; Lin et al., 1998; Vik et al., 1984; Lin and Peng, 1996; Pouet and Grasmick, 1995; Lin and Peng, 1994; Tsai et al., 1997; Naumczyk and Zilio-Grondi, 1996; Kovatcheva and Parlapanski, 1999). In addition, Koparal and Ögütveren (2002) studied removal of nitrate from water by electroreduction. Electrocoagulation has been attracting special interest in all applications of electrochemical treatment for the purification of wastewater.

In the present paper, we have conducted an experimental investigation of treating paper mill effluents by using the electrochemical method. The effects of several experimental parameters such as current intensity, electrode type (Al and Fe) and electrolysis time on the removal of lignin and phenol from paper mill effluents by the electrocoagulation method have been examined.

2. Materials and methods

2.1. Characterization of the paper mill effluents

The paper mill effluents utilised for this study were taken from a modern bleached kraft mill located in western Turkey. Wastewater (4500 m³/h) are discharged into Gökova gulf (Muğla, Turkey) by deep discharging after being collected in sedimentation pools and aerated for a week. The wastewater samples used in this study were taken from aerated lagoons right before the sea discharging process. The characteristics of the raw wastewater are given in Table 2.

Table 2
Characteristics of bleach Kraft mill effluents

Parameter	Value
Colour	Brown
pH (average)	7.50
Compounds (mg/L)	
PO ₄ ³⁻	0.176
NO ₂ ⁻	0.213
NO ₃ ⁻	0.183
NH ₄ ⁺	9.881
Phenol	0.535
Lignin	13514.0
BOD	25.52
COD	426.03

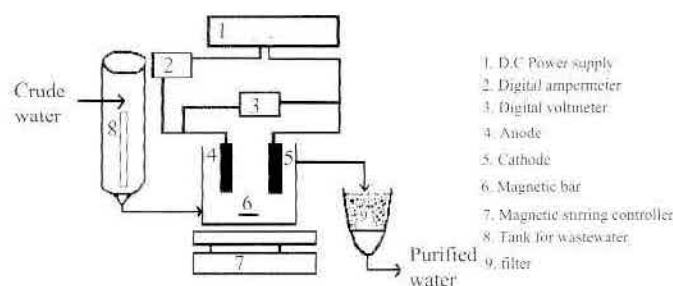


Fig. 1. Experimental apparatus used in this study.

2.2. Experimental set-up and measurements

Iron and aluminium plates (4.0 cm × 4.0 cm) were used as electrodes. In the electrochemical processes, the electrode material is essential. Iron and aluminium electrodes were used in the electrocoagulation because they are cheap and their production is very simple (Inan et al., 2004). The electrodes were washed with HCl solution (15% W/V) before each run. Following each run, the electrodes were washed with distilled water, dried and used again. The same experiments were carried out with both electrodes in order to compare the results. The anode–cathode distance was kept constant (2.0 cm). The experimental apparatus used is given in Fig. 1.

All experiments were performed at a constant temperature of 21–22 °C at 200 rpm stirring speed. In each run, 250 cm³ of wastewater solution was placed into the electrolytic cell. The electrolyte (NaCl) concentration of 0.2 g was kept constant initially. Cell voltage and current were measured by a Keithley 2010 digital multimeter and a Topward Dual-Tracking DC 6303D was used as the power supplier. In the experiments in which cell voltages were kept constant at 12 V, a small variation in the steady current was observed. Electrolysis time, current density and electrode type were selected as parameters. The current density was changed by increasing the input voltage, provided that the distance between the electrodes was kept constant. At the end of the experiments, the treated

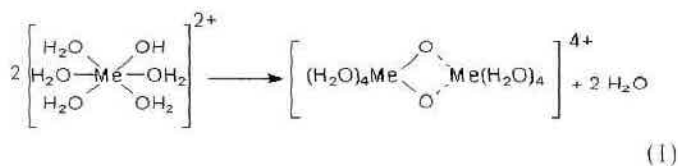
solution was filtered by using Whatman No 40 filter paper. The measurements of BOD₅, COD, phenol and lignin concentrations before and after electrocoagulation were done to calculate the removal of BOD₅, COD, phenol and lignin and to determine the quality of the treated wastewater. All experiments were repeated twice, and the experimental error was around 4%. The concentrations of phenol and lignin were determined spectrophotometrically (Dr. Lange spectrophotometer) by analysis of the colour resulting from the reaction of phenol with 4-aminoantipyrine and from the reaction of lignin with folin phenol reagent (tungstophosphoric acid) at 500 and 700 nm, respectively (Eaton et al., 1995). The detection limits of the method were in the range of 0.03–6.4 mg/L. The dichromate method (Standard Methods, Section 5220D, Eaton et al., 1995) was used to determine COD. The measurements were carried out spectrophotometrically in the range of 100–2000 mg/L (605 nm). The measurements for (BOD₅) were done by diluting 100 mL of the wastewater with 1 L distilled water and determining the amount of soluble oxygen according to the Winkler method (Eaton et al., 1995).

3. Results and discussion

3.1. The effect of treatment time

The efficiencies of lignin, phenol, COD and BOD removal at the different electrolysis times (1.0, 2.5, 5.0 and 7.5 min) at a constant cell voltage (12.0 V) and at a constant current (77.13 mA) were investigated for both types of anodes. In paper mill effluents, as was stated in the early studies, the brown colour of the effluent results from the presence of lignin (Diez et al., 1999). When the Al electrode was used for removal of lignin, initially a fast increase was observed with increasing electrolysis time. After 2.5 min of electrolysis time, the lignin removal reached 80% for each electrode. In addition, the time required for maximum lignin removal with the Al electrode was shorter than that with the Fe electrode (see Fig. 2). After this time, the percentage of lignin removal for both electrodes remained approximately constant.

It is known that the hydrolysis products of Al³⁺ and Fe³⁺ are responsible for the effects observed during particle aggregation; polymerisation as depicted in the following formula will usually take place:



The possible combinations of various hydrolysis products are endless and one or more of them may be responsible for the observed action of aluminium or iron (Uğurlu, 2003, 2005).

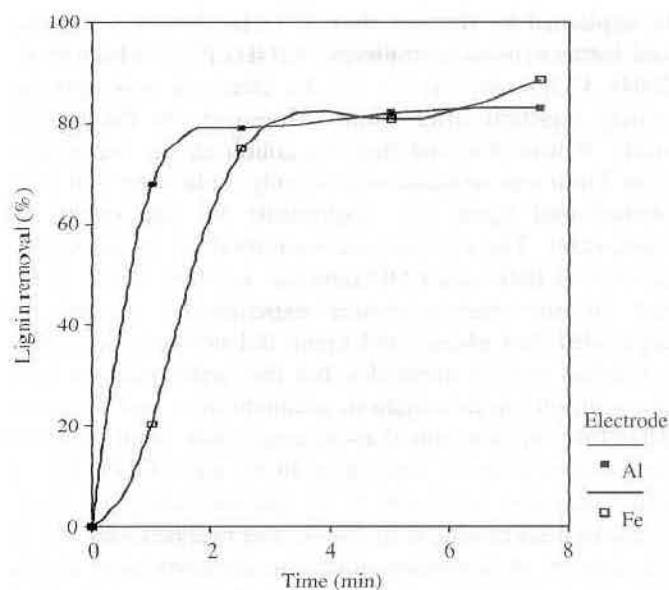


Fig. 2. Lignin removal as a function of time (cell potential: 12 V, initial suspension pH: 7.6).

In experiments in which Al is used as the anode, the electrogenerated aluminium ions may form monomeric and polymeric hydroxo-complexes, depending on the pH range. These complexes have a tendency to polymerise in the pH 4–7 range. Over saturation and formation of the amorphous hydroxide precipitate $\text{Al}(\text{OH})_3(\text{H}_2\text{O})_{3(\text{s})}$ enmeshes colloidal particles in a “sweep floc”. Many monomeric and polymeric species such as $\text{Al}(\text{OH})_2^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}_2(\text{OH})_4^{3+}$, $\text{Al}(\text{OH})_4^-$, $\text{Al}_6(\text{OH})_{15}^{3+}$, $\text{Al}_7(\text{OH})_{17}^{4+}$, $\text{Al}_8(\text{OH})_{20}^{4+}$, $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$, and $\text{Al}_{13}(\text{OH})_{34}^{5+}$ have been reported (Gürses et al., 2002). When an Al anode is at an anode–cathode distance of 2.0 cm and at an electrolysis of 3 min, monomeric hydrolysis products ($\text{Al}(\text{OH})_2^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}_2(\text{OH})_4^{3+}$) mainly exist in the medium. Under these conditions, electrostatic charge neutralisation between these hydrolysis products and hydrolysed negatively charged organic molecules occurs. Because of this process, the aggregation tendency of the monomeric hydrolysis products increases. As can be seen from Fig. 2, at the end of this time (3 min), a small amount of lignin is adsorbed onto the aggregates. In addition, the results indicate that formation of coagulate depends on the structures of the contaminants, and so, on the ability of contaminant molecules to be absorbed on hydrolysis products or flocs.

For a Fe electrode, Gürses et al. (2002) reported that electrogenerated ferric ions may form monomeric ions, ferric hydroxo complexes with hydroxide ions and polymeric species, namely, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$, $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^{1+}$, $\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$ and $\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_4^{2+}$, depending on the pH range. When a Fe electrode is used, the amount and the variety of hydrolysis products formed by anodic dissolution depend significantly on electrolysis time. Formation rates of the different species play an important role in removal of the contaminants. Considering the above explanations of the removal process of lignin

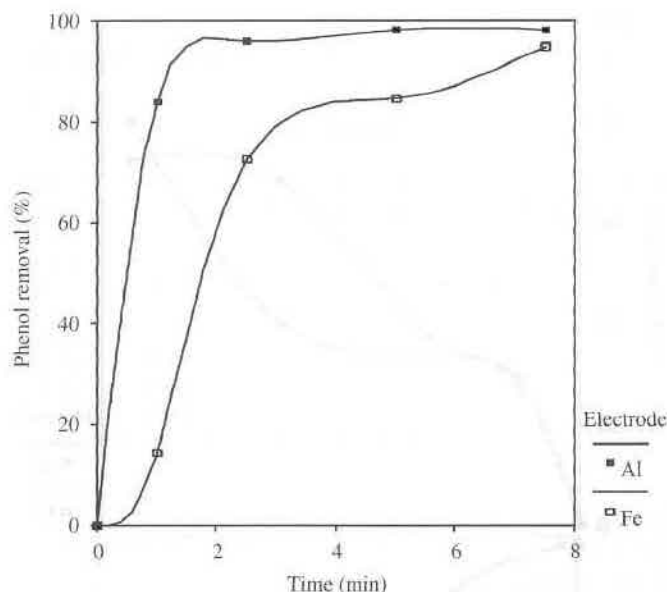


Fig. 3. Phenol removal as a function of time (cell potential: 12 V, initial suspension pH: 7.6).

and phenol, it can be assumed that lignin and phenol are captured and removed by flocculation, by sedimentation or owing to the highly dispersed ferric and/or aluminium hydroxide micro flocs in the bulk and gas evolving at the cathodes by H_2 flotation during electrolysis.

The results obtained for phenol removal at different times are shown in Fig. 3. For the Al electrode, the phenol removal increased slowly after 2 min. In the case where the Fe electrode was used, the phenol removal increased very fast up to an electrolysis time of 3 min (max. 92%) as revealed by Fig. 2. The highest phenol removal (99%) was observed after 7 min. It is thought that increasing electrolysis time improved the efficiency of removal by inducing faster aggregation of the hydrolyse products. The fact that some Fe^{3+} ions were dissolved from the anode surface and that the solids contained iron, and taking into account the characteristics of the solids, it seems reasonable that these compounds were formed by electrochemically assisted processes involving the organic compounds present in the waste (phenol and organic intermediates) upon treatment with ferric ion. It has been reported that phenol and organic acids can interact chemically with trivalent cations to form insoluble species by combined complexation, precipitation, and/or coagulation processes (Canizares et al., 2002). Moreover, phenol and similar organic compounds have a tendency to move towards aqueous solution. As a result of chlorine usage in many phases of the paper bleaching process, chlorinated lignin and phenol compounds are expected to be present abundantly in the effluents and as they have non-polar features, and they are thought to adsorb to hydrolyse products occurring as a result of the electrolysis process. Some of the small organic molecules and the suspended solids are captured by $\text{Fe}(\text{OH})_3$ or $\text{Al}(\text{OH})_3$ and the other monomeric and

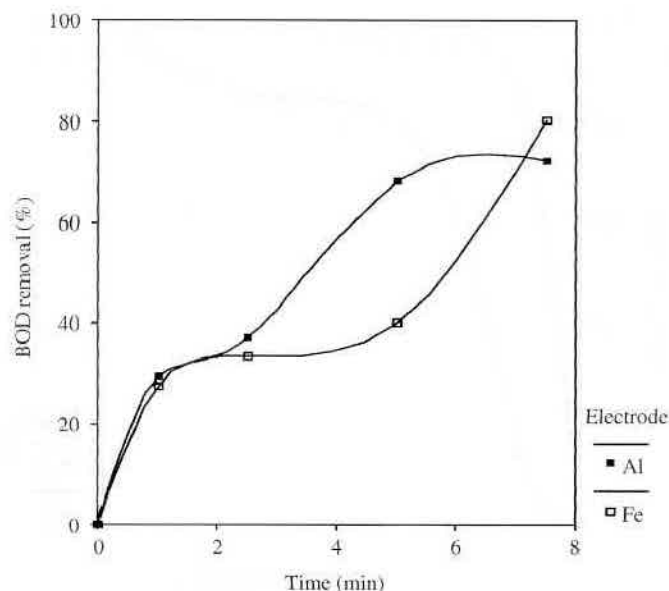


Fig. 4. BOD removal as a function of time (cell potential: 12 V, initial suspension pH: 7.6).

polymeric hydroxides are removed by sedimentation or H_2 flotation (Gürses et al., 2002).

As seen from Fig. 4, BOD removal for both anodes (Al and Fe) was the same until 2 min. However, with increasing time, the rate of BOD removal obtained with the Al electrode (the max. BOD removal was 80%) was higher than that with the Fe electrode (65%). Although the percentage of BOD removal for the Al electrode tended to become constant after 5 min, the percentage of BOD removal for the Fe electrode increased with increasing time. A major contribution towards BOD is expected from dissolved organic substances. Generally, strong oxidising agents such as hydrogen peroxide are used to oxidise the dissolved organic molecules. The removal of COD and BOD by electrocoagulation could be attributed to the removal of suspended solids and to precipitation of dissolved organic molecules as organometallic compounds. However, detailed studies on oxidation–reduction reactions on the surface of the electrodes and in the bulk phase are essential to establish the mechanisms of electrochemical removal of COD (Murugananthan et al., 2004).

Fig. 5 shows the COD removal as a function of the treatment time. The change in COD removal with various times (1.0, 2.5, 5.0 and 7.5 min) was investigated by applying a constant cell voltage (12 V) to both electrode materials. In general, the graphs of COD removal versus retention time demonstrate an increasing trend. At 1 min retention time, aluminium provided approximately 45% COD removal versus 32% for iron; for the 7.5 min retention time the corresponding values were 75% (Al) and 55% (Fe). Due to the high pH of the wastewater (7.6), Fe^{3+} ions that were dissolved from the anode precipitated to form $Fe(OH)_2$ and $Fe(OH)_3$. The organic complexes formed by the interaction of phenol with the surface of this precipitate. Aluminium anodes behave differently. This can

be explained by the fact that $Al(OH)_3$ dissolves in water and forms hydroxo complexes $[Al(OH)_n]^{(n-3)-}$ (Inan et al., 2004). COD removal for the Fe electrode was approximately constant after 5 min. Moreover, in the present study, it was observed that the colour in the wastewater after 2 min was reduced considerably, indicating that both phenol and lignin are responsible for the colour of wastewater. These results are supported by the increasing amount of BOD and COD removal. In other words, at the end of the electrochemical experiments, it may be concluded that phenol and lignin did not turn into other colourless organic molecules, but they were removed from the solution via flocculation, sedimentation and flotation. Therefore, the plateaus that occurred after 2 min retention time in the curves for removal of BOD₅ and COD in Figs. 4 and 5 may also be related to the size and selectivity of the hydroxo flocs produced by the Al and Fe electrodes and/or the amount of remaining phenol in the suspension during this time. In addition, the phenol, lignin and other components in the paper mill effluents can be considered as the fraction of slowly biodegradable COD and soluble inert COD. The fractions of soluble slowly biodegradable and the inert COD in wastewater contain typically the bulk of the organic matter present in domestic wastewater and dissolved humic or fulvic acids (Hu et al., 2002).

The apparent kinetics of COD, lignin, phenol and BOD₅ removal can be expressed as the following pseudo-first-order rate equation:

$$\ln \frac{[C]_t}{[C]_0} = -kt, \quad (2)$$

The slope of the plot of $\log C_t/C_0$ versus time gives the value of the rate constant k , min^{-1} . Here, C_0 is the initial concentration in milligrams per litre, and C_t is the concentration value in milligrams per litre at time t .

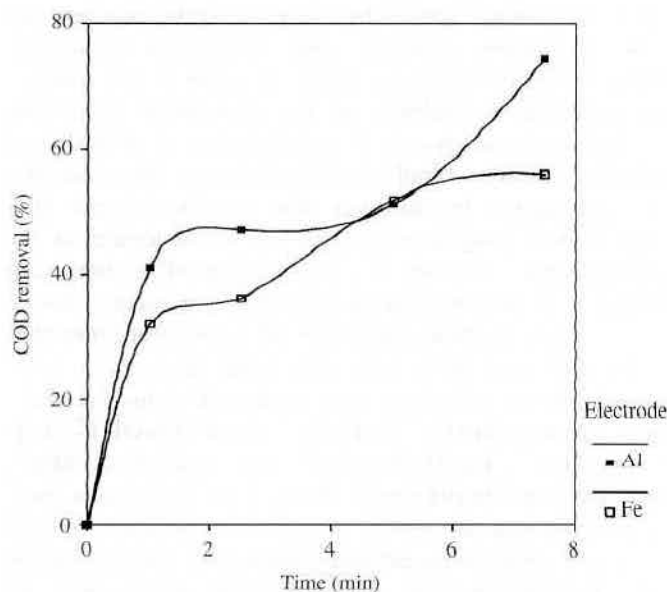


Fig. 5. COD removal as a function of time (cell potential: 12 V, initial suspension pH: 7.6).

Table 3

Summary of the kinetic and other properties of the paper mill effluents by the electrocoagulation method (cell potential: 12.0 V and initial suspension pH: 7.6 and 5 min)

Compounds	Initial concentration (mg/L)	Final concentration (mg/L)		Kinetics				Energy consumption			
				Rate constant k' (min ⁻¹)		r^2		kWh/kg of compound		kWh/m ³ of compound	
		Fe	Al	Fe	Al	Fe	Al	Fe	Al	Fe	Al
COD	426.12	198.04	206.31	0.085	0.118	0.99	0.81	0.6	0.5	0.136	0.105
BOD	25.53	15.31	6.38	0.119	0.159	0.80	0.91	11.0	5.1	0.113	0.091
Lignin	13,514.00	2650.07	2702.14	0.086	0.281	0.92	0.89	7.13×10^4	7.15×10^4	96.25	95.52
Phenol	0.535	0.091	0.017	0.456	0.335	0.99	0.90	17.37×10^4	14.89×10^4	92.93	79.66

The above equation may be of the type $y = mx$ and a line plot of $\ln C_t/C_0$ versus t indicates that the electrocoagulation process follows a first-order reaction (Table 3). Table 3 provides the rate constant (k), and respective r^2 values for phenol, lignin, COD and BOD₅ removal.

3.2. The effect of current intensity

It is well known that current determines not only the coagulant dosage rate but also the bubble production rate and the size and growth of flocs which can influence the treatment efficiency of the electrocoagulation. Therefore, the effect of current intensity on the pollutant removal was investigated (Adhoum and Monser, 2004). The phenol, lignin, BOD and COD removals from the paper mill effluent were measured for 5 min at different current intensities (25.50 and 75.0 mA). The effect of the current intensity on the treatment efficiency of the electrochemical process has been investigated for different wastewaters (Lin and Peng, 1994). With sufficient power supply, phenols, like other organic compounds, are reduced at the cathode to smaller molecules (Pletcher and Walsh, 1990; Savall, 1995; Lin et al., 1998). During the electrochemical experiments, the small amounts of sludge were scraped off from the top and the bottom of the electrolytic cell, and were evidence of the sedimentation and flotation action.

Since the total surface area of the electrodes was about 16 cm², the applied current was readily converted to the current density. Therefore, the removal of phenol, lignin, BOD₅, and COD were graphed against current density in Figs. 6–9. Fig. 6 depicts the phenol removal efficiency as a function of current density. The percentage of phenol removal up to approximately 2.5 mA/cm² was the same for both the Al and Fe electrodes. However, there was an increase in phenol removal by the Al electrode with increasing current density compared with the Fe electrode. As expected, it appears that for a given time, the removal efficiency increased significantly with increased current density. This is attributed to the fact that at high current, the amount of aluminium oxidised increased, resulting in a greater amount of precipitation (Adhoum and Monser, 2004).

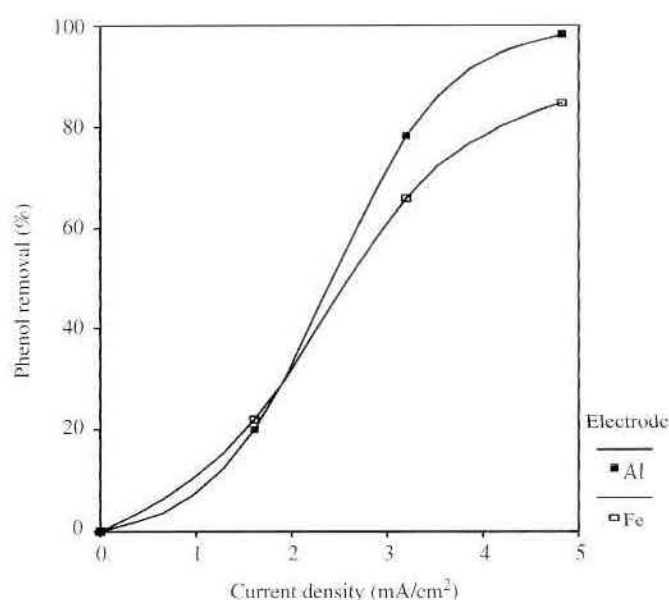


Fig. 6. Effect of current density on phenol removal (time: 5 min).

When Al and Fe electrodes were used at different current densities (1.6 and 4.7 mA/cm²) for lignin removal, an increase was observed (Fig. 7). The percentage of lignin removal for the Al electrode was higher than that for the Fe electrode at low current densities. The Al electrode revealed a tendency for steadiness after 1.9 mA/cm². However, in the case of the Fe electrode, a fast removal up to 3.1 mA/cm² and then gradually slowing removal was observed. At approximately 5 mA/cm², the same removal efficiency of 80% was obtained for both electrodes. At low current densities, BOD removal by the Al electrode was higher than that by the Fe electrode (Fig. 8). For the Al electrode, as the current density increased, BOD removal also increased. At higher current densities, the supply of aluminium ions was generated rapidly compared to the coagulation process, resulting in a decrease in removal efficiency calculated on an equivalent aluminium basis. In addition, the faster removal of aluminium hydroxide from

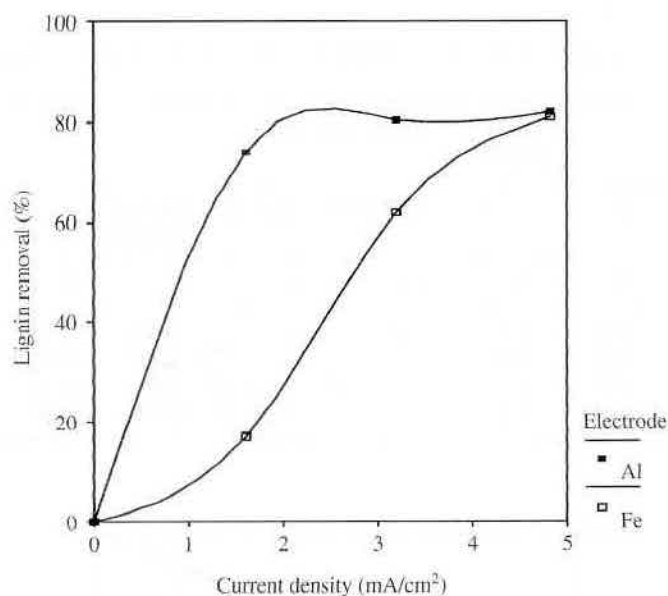


Fig. 7. Effect of current density on lignin removal (time: 5 min).

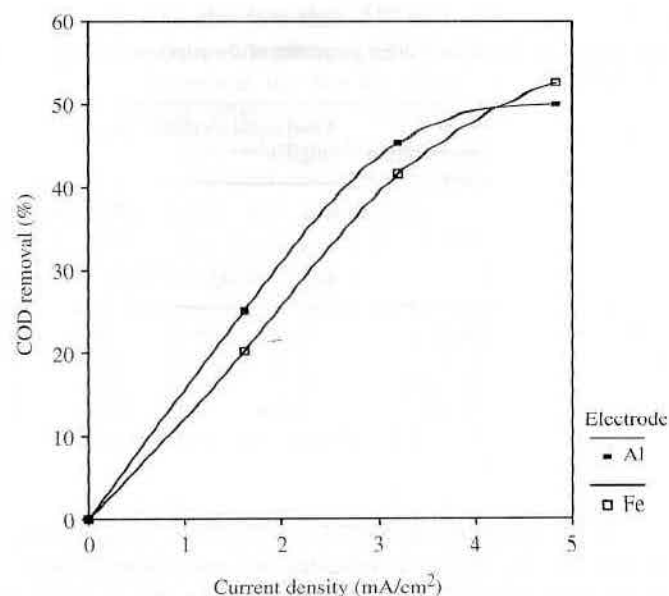


Fig. 9. Effect of current density on COD removal (time: 5 min).

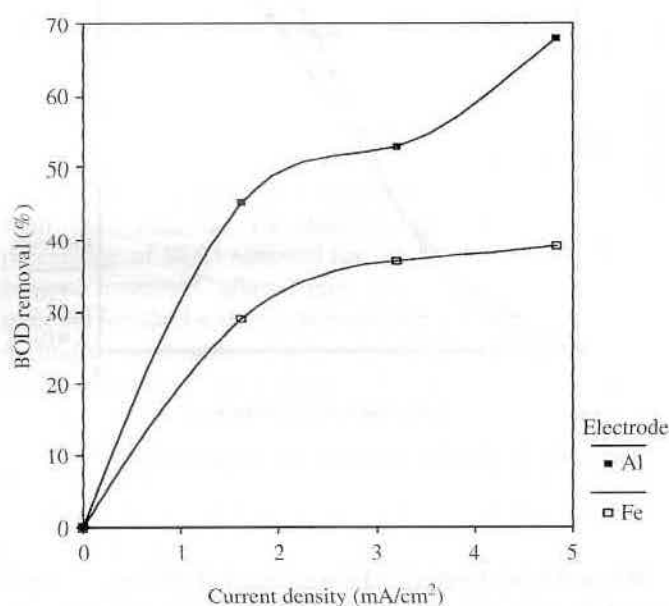


Fig. 8. Effect of current density on BOD removal (time: 5 min).

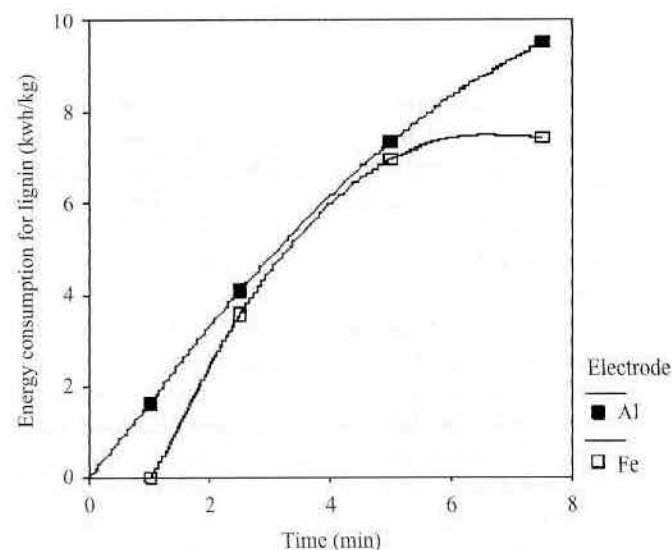


Fig. 10. Energy consumption on lignin removal as a function of time (cell potential: 12.0 V and initial suspension pH: 7.6).

solution by flotation leads to a reduction in the probability of collision between the pollutant and coagulant (Adhoum and Monser, 2004). However, for the Fe electrode at 1.9 mA/cm², a steadiness (40%) was observed.

Both the electrodes showed similar behaviour for COD removal at low current densities. The results are given in Fig. 9. The same efficiency of COD removal (50%) was found at approximately 4.4 mA/cm². A very small decrease with increasing current density was observed. Chen et al. (2000) reported that when organic pollutants in effluents were treated by electrochemical methods, COD removal and colour removal increased with increasing current intensity. Higher removal related to the experiments carried out at different current densities can be explained

based on a decrease in electric resistance of solution and an associated increase in the transfer speed of organic and inorganic species to the electrodes.

3.3. Energy consumption

Considering the initial and final concentrations of compounds in the paper mill effluent at different times, the electric energy (EE) consumed to remove 1 kg of each compound (phenol, lignin, COD and BOD) was calculated with the following equation (Kestioğlu et al., 2005).

$$EE \text{ (kWh/kg of compound)} = \frac{VI \cdot 1000}{60(C_0 - C_1)} \quad (3)$$

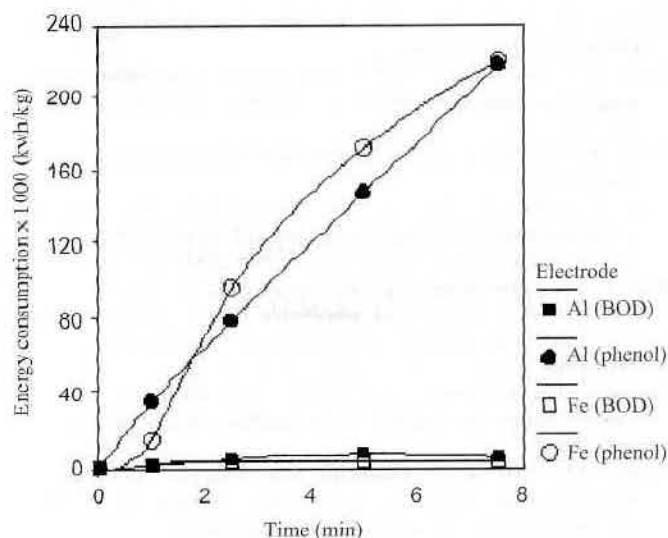


Fig. 11. Energy consumption on BOD and phenol removal as a function of time (cell potential: 12.0 V and initial suspension pH: 7.6).

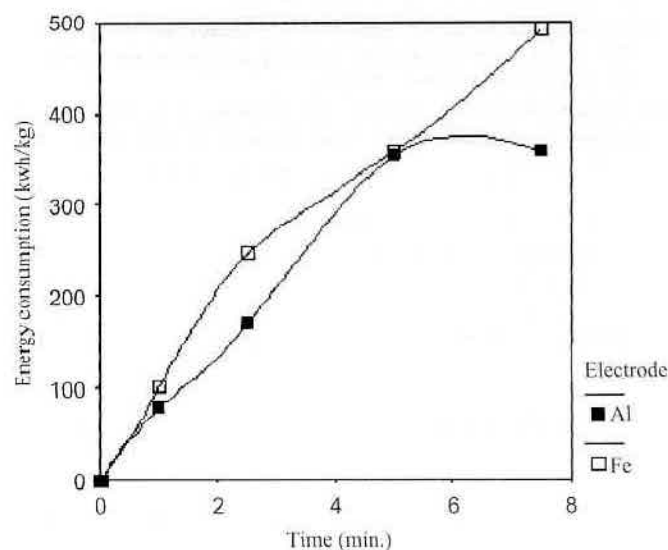


Fig. 12. Energy consumption on COD removal as a function of time (cell potential: 12.0 V and initial suspension pH: 7.6).

where V is the applied voltage (V), I the current amount (A), t the electrolysis time (min), C_0 the initial concentrations (g/L) and C_t is the concentration value of compounds (g/L) at time t . The results obtained are plotted in Figs. 10–12. These results indicate that the various organic compounds in the paper mill effluent had different energy consumptions. For lignin the rate of energy consumption increased linearly with the Al electrode, but for Fe the energy consumption was approximately constant between 5.0 and 7.5 min. Research suggests that there are 280 well-defined organic and inorganic compounds in wastewater coming from paper mills (Uğurlu et al., 2005). Consumption of less energy for BOD removal than for removal of lignin and phenol can be explained by its low concentration in the wastewater (Table 2).

4. Conclusions

In the present work, the electrocoagulation efficiency for the removal of lignin, phenol, BOD and COD has been investigated. The influence of variables such as cell voltage, current intensity and electrolysis time on the removal of lignin, phenol, BOD and COD has been determined. As discussed in the text, the importance of the variables in the electrocoagulation process can be explained based on the pronounced dependence of the hydrolysis species on current density and electrolysis time. The optimum values of the variables, such as electrolysis time, applied voltage and current density, on the removal of these pollutants for both electrodes are determined as 2 min, 12.0 V, and 4.8 mA/cm^2 , respectively. However, it was found that for BOD and COD removal a little bit more time was required. When the effect of the current intensity on the removal of lignin, phenol, BOD and COD was examined, as was expected, an increase in removal efficiency was observed with increasing current intensity. In addition, it was observed that a range of $2.5\text{--}5 \text{ mA/cm}^2$ was sufficient for the removal of the pollutants mentioned above.

Electrochemical methods can be said to be promising for treatment of paper industry wastewater.

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Modeling water and sediment contamination of Lake Pontchartrain following pump-out of Hurricane Katrina floodwater

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Abstract

Levee failure and overtopping as a result of Hurricane Katrina caused major flooding of New Orleans, Louisiana. Floodwaters, which were contaminated with heavy metals, organic chemicals, and fecal coliform bacteria (FCB), were pumped into neighboring Lake Pontchartrain during dewatering. The impact of levee failure on water and benthic sediment concentrations in the lake was investigated by applying a numerical water quality model coupled to a three-dimensional, numerical hydrodynamic model. The model was used to compute water and benthic sediment concentrations throughout the lake for lead, arsenic, benzo(a)pyrene (BaP), and 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene (DDE), and water concentrations for FCB. Computed concentrations resulting from actual pumped discharges with levee failure and overtopping were compared to computed concentrations resulting from pumped discharges without levee failure or overtopping, and concentrations from both sets of conditions were compared to ecological water and sediment quality screening guideline values. The model indicated that incremental increases above pre-Katrina benthic sediment concentrations are about a factor of 10 greater with dewatering of the floodwaters than with dewatering of storm water without flooding. However, these increases for the metals are small relative to pre-Katrina concentrations. The results showed that the ecological screening-level sediment quality guideline values were exceeded for BaP and DDE in areas near the south shoreline of the lake as a result of floodwater pump-out, whereas, this was not the case for storm water removal without flooding. The model showed that lake water column concentrations should be about the same during both dewatering conditions regardless of whether there is flooding or not.

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Keywords: Lake Pontchartrain; Hurricane Katrina; Floodwaters; Levee failures; Modeling; Contaminants; Sediments

1. Background

On August 29, 2005, the storm surge associated with Hurricane Katrina resulted in the failure and overtopping of levees protecting New Orleans. Floodwater was pumped out of the city into surrounding marshes and Lake Pontchartrain over a period of 37 days, introducing contaminants to the surrounding environment and raising environmental concerns. Trace metals, organic chemicals, and bacterial contamination were measured in New Orleans floodwater shortly after the hurricane and flood event (Pardue et al., 2006; Presley et al., 2006; US EPA, 2006). The Interagency Performance Evaluation Task Force (IPET) led by the US Army Corps of Engineers

was charged to study and understand the behavior of the New Orleans hurricane protection system in response to Katrina. The IPET was in part tasked with evaluating the socio-economic consequences of levee failures, including environmental consequences. This paper describes the numerical modeling for IPET to evaluate contamination of Lake Pontchartrain resulting from dewatering following Katrina as contrasted with dewatering without levee failures and overtopping.

2. Approach

The three-dimensional (3D) hydrodynamic model CH3D-WES (Johnson et al., 1991, 1993) and the 3D water quality model CE-QUAL-ICM (ICM) (Cercio and Cole, 1995) were used to model conditions in Lake Pontchartrain for a period of 90 days starting on September 1, 2005.

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Contaminant concentrations were modeled for two conditions: (1) dewatering of floodwaters for the “*actual*” conditions that occurred with levee breaches and overtopping; and (2) dewatering for conditions of the system performing as designed and without levee overtopping (“*baseline*” conditions). The *baseline* conditions served as a basis for comparison with the *actual* conditions. Both the *actual* and *baseline* conditions include the period during which pumps were operating to remove flood and rain water from the city following Hurricanes Katrina and Rita.

2.1. Hydrodynamic model

The *z*-plane version of CH3D-WES was used. This version has a varying number of layers with the total number along a water column depending on the depth. A plan view of the model computational grid is shown in Fig. 1. The grid contained 6038 computational cells in the surface layer and 21,018 cells in total over all layers. Each layer thickness was 1.52 m except the surface layer, which varied depending on the water surface elevation. The maximum number of layers was six for a maximum depth of about 9.14 m. A typical grid cell size in plan form was on the order of 300 m × 700 m. The grid was generated using a grid generation tool within the Surface Water Modeling System (<http://chl.erdc.usace.army.mil/chl.aspx?p=s&a=Software;4>). National Oceanographic and Atmospheric Administration (NOAA) navigation charts were used to develop the bathymetry with 5 ft intervals.

Although the CH3D-WES model includes baroclinic terms to simulate stratified flows resulting from water density differences caused by temperature and salinity, this feature was not activated for this study since the floodwaters had about the same salinity as the lake water in the vicinity of the pumped discharges. In the month following the storm, salinity measurements taken in the lake at

Station 4 (south shore at Pontchartrain Beach) by the Lake Pontchartrain Basin Foundation averaged 7.4 parts per thousand (ppt), whereas, salinity measurements taken in the New Orleans floodwaters averaged 5.6 ppt. Floodwater salinity was higher near the lake shore (ranging approximately from 7 to 9 ppt) and decreased moving south towards downtown away from the shore (ranging approximately from 2 to 6 ppt).

The hydrodynamic model was run for both the *actual* and *baseline* conditions, where the differences between the two conditions were the pumping rates and durations. Wind speed and direction from the New Orleans International Airport was applied to the model. Tide records from NOAA were used as boundary conditions at the open sea boundary, which was located at the Rigolets (see Fig. 1), the inlet between Lake Pontchartrain and Lake Borgne, which connects to the Gulf of Mexico. Additionally, the pumped flows were applied as boundary conditions along the south shore and were a major forcing function for the lake hydrodynamics during *actual* dewatering. Freshwater stream flows entering the lake were not included in the model since most streams enter along the north shore and are a minor forcing component compared with wind and tidal forcing and pumped flows, except when Mississippi River floodwaters are diverted through the Bonne Carre Spillway.

The hydrodynamic model used the estimating pumping rates obtained from IPET task team 8 (Pumping Station Performance) for *actual* conditions of post Katrina, including the pumping during and following Hurricane Rita. These data show that the pumps started operating on September 11, 2005, and ended on October 17 for pump-out to the lake. Obtaining pumping rates for the *baseline* conditions was more problematic. Other IPET tasks will estimate the pumping rates for conditions of the levees performing as designed, but this information was not available at the time of this study. In the absence of these

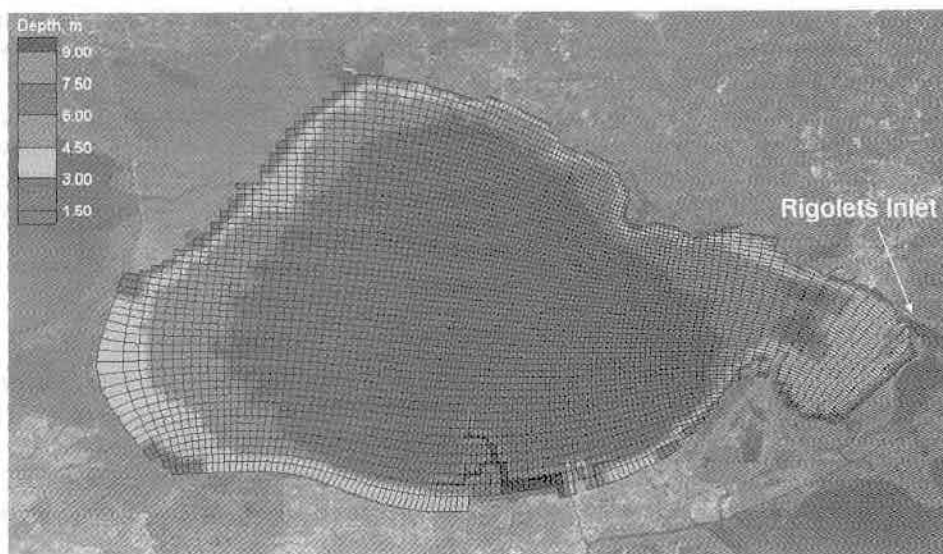


Fig. 1. Model grid for Lake Pontchartrain with depth contours.

data, assumptions were used to establish a *baseline* condition. The rainfall amounts recorded for Katrina and Rita were multiplied by the approximate rainfall collection area to produce rainfall volumes. The known pump flow capacities were divided into the rainfall volumes to estimate the time required to pump out the rainfall. The capacity of each pump was used with the duration required to dewater the rainfall to establish the *baseline* pumped flows. This approach does not include water that overtopped the levees. Thus, this approach assumes that a levee system was in place that fully protected New Orleans from any storm surge flooding by these two hurricanes.

2.2. Water quality model

The water quality model was originally developed during an eutrophication model study of Chesapeake Bay (Cерco and Cole, 1993), but has subsequently been applied to other systems in the US (Cерco et al., 1994, 1999, 2000) and the San Juan Bay and Estuary in Puerto Rico (Bunch et al., 2000). The version of the model used for Lake Pontchartrain was based on a recent version used for Lake Washington, WA (Cерco et al., 2004, 2006; Kim et al., 2006).

During the Lake Washington model study, the ICM model code was modified for simulating a pathogen and two toxicants. The two toxicants were coded in a generalized format and were intended to provide a rapid screening tool and a foundation for more detailed formulations that could be added later. The two toxicants are subject to identical processes including degradation, volatilization, partitioning to solids, settling, and burial. A mass balance of toxicant within the water column and sediment bed is maintained. Toxicant 1, which can represent a metal, partitions to inorganic solids, and toxicant 2, which represents an organic chemical, partitions to particulate organic carbon (POC). Degradation can occur in both the water column and sediments. Dissolved toxicant diffuses in either direction across the sediment–water interface. Linear, reversible, equilibrium partitioning to solids is assumed, and the fractions of dissolved and particulate toxicant are computed accordingly. The sediment bed for toxicant mass balance is treated as a single, well-mixed layer. Degradation in the bed is applied to the bulk (total) contaminant concentration. Degradation rates and partition coefficients within the sediments may vary from those specified for the water column. The mass balance and partitioning equations for toxicants within the water column and sediment are presented by Cerco et al. (2004).

The water quality model used the same grid resolution as the hydrodynamic model of Lake Pontchartrain. The hydrodynamic model was executed, flow fields were saved, and these data were subsequently used to provide flow fields required by the water quality model.

The water quality model was applied for five constituents, arsenic (As), lead (Pb), benzo(a)pyrene (BaP), 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (DDE), which

is a degradation product of DDT, and fecal coliform bacteria (FCB). Chemicals from various classes (e.g., pesticides, polycyclic aromatic hydrocarbons, and metals) were selected to be representative of other compounds. The chemicals selected for the modeling effort were identified from existing analytical chemistry data for soils and waters in New Orleans during the flooding event. Chemicals were selected based on their frequency and magnitude of detection, association with suspended particles, and potential to cause adverse ecological impacts. The model state variable for each contaminant was treated as total concentration (i.e., dissolved and particulate) with fractions of dissolved and particulate calculated from equilibrium partitioning to suspended solids and sediment bed solids. Fate processes of sorption to solids, settling of particulate contaminant, volatilization of dissolved contaminant, and die-off of FCB were modeled. Degradation of the organic chemicals was ignored given the relatively short simulation period and long half-life of these compounds in natural waters. These constituents provide a wide range in adsorption behavior for inorganic and organic contaminants with arsenic having a relatively low sorption distribution coefficient and DDE having a high value.

The water quality model requires constituent loading (mass/time) for each effluent location. Loading is the product of discharge rate (volume/time) and concentration (mass/volume) of the effluent. With pumping rates given, the concentrations of the effluent had to be determined for both scenarios. Fortunately, for the *actual* scenario, many floodwater and flood sediment samples had been collected and analyzed for a host of contaminants. These data were collected by the US Environmental Protection Agency (EPA), Louisiana State University (LSU), US Geological Survey (USGS), and Louisiana Department of Environmental Quality (DEQ) and were assembled into an EPA database (US EPA, 2006). Other sources of data included peer-reviewed publications of studies reporting similar information (Pardue et al., 2006; Presley et al., 2006). Data for the constituents assessed in this study were assembled in a database and analyzed to yield a median concentration and a 95% upper confidence limit (95UCL) concentration for each constituent for three different areas of interest, Orleans Parish Metro, Orleans Parish East, and St. Bernard Parish. The first two areas involve floodwaters that were pumped into the lake, and the latter represents floodwaters that were pumped into Violet Marsh. Given the extensive difficulty in trying to sort out which specific sub-areas of floodwater (and associated sample concentrations) to assign to each pump, the decision was made to process all measured values within each of the three broad areas to produce a single median and 95UCL concentration to use for the pumped effluents of that area. Any measurements that were below detection limit were set equal to 1/2 the detection limit rather than zero for the analysis. In summary, measured concentrations were used to establish the pumped loadings discharged into the lake

for the *actual* conditions for Orleans Metro and Orleans East, and the concentrations were held constant for the duration of the pumping to establish those loadings.

The original plan for estimating pumped concentrations for the *baseline* conditions was to use data from a previous pumping event that endured rainfall of the amount that fell during Katrina. However, no such observed data could be found for the constituents being studied. Pardue et al. (2006) stated that the metal concentrations in the Katrina floodwaters of New Orleans were typical of storm water with a few exceptions of elevated concentrations of lead. Jin et al. (2004) reported FCB concentrations on the order of 40,000 MPN/100 mL measured during 1998 in pumped storm water in drainage canals that empty into the lake. This concentration is within the range of values measured in the Katrina floodwaters. Given these previous findings and the lack of any better information, the assumption was made that the pumped concentrations for the *baseline* conditions would be the same as those for the *actual* conditions. However, the total constituent mass discharged for the *baseline* conditions is considerably less since the pumps operate for a much shorter period of time to remove far less water.

Output from the 3D lake water quality model consists of time-varying concentrations in the water column for each computational cell and time-varying sediment concentrations in the benthic sediment layer beneath each bottom water cell. Such a large amount of data requires reduction to render presentations that are useful for interpretation. Two-dimensional contour plots of maximum concentrations in the water surface layer and benthic sediment layer were used to collapse data for manageable interpretation.

3. Model input

3.1. Parameters and basic data

In addition to boundary conditions and model control variables, several parameters and basic data are required to apply the lake model, which include:

- total suspended solids (TSS) (mg/L),
- TSS settling rate (m/day),
- FCB die-off rate (day^{-1}),
- fraction of total organic carbon (TOC) to total sediment dry weight, f_{oc} , for the water column and sediment bed,
- sedimentation variables, either burial rate or resuspension rate (m/day),
- benthic surficial layer porosity,
- sediment–water sorption distribution coefficient, K_d (L/kg).

TSS was calculated from turbidity using a regression developed from data collected from the New Orleans Inner Harbor Navigation Channel (IHNC) as part of the study (Estes et al., 2006) of the Corps Dredged Material Management Units (DMMU). Abundant turbidity data

existed for both the floodwaters and the lake. TSS settling rate was set to 1 m/day based on experience in modeling similar systems and particle settling studies conducted for the IHNC. The total coliform bacterial die-off rate is typically around 1.0 day^{-1} (Thomann and Mueller, 1987) for freshwater and 1.4 day^{-1} for seawater. Jin et al. (2004) measured FCB die rates of approximately 2.8 day^{-1} in the lake. The relatively conservative value of 1.0 day^{-1} was used in the model. Data from the DMMU studies indicated f_{oc} values of about 0.02. Resuspension was assumed to be zero; using the settling rate, TSS, and sediment porosity to compute sediment bulk density, a burial rate of 0.026 m/yr was calculated based on a steady-state solids balance. Benthic surficial layer porosity was assumed to be 0.9, which is a value typical of most unconsolidated surficial sediments. Estimates of K_d for arsenic and lead were obtained from the literature and consisted of 300 and 4000 L/kg , respectively. The organic carbon–water partition coefficient, K_{oc} , was computed for the organic constituents BaP and DDE using the relationship (Karickhoff et al., 1979):

$$K_{oc} = 0.6 K_{ow}, \quad (1)$$

where K_{ow} is the octanol to water partition coefficient for organic chemicals. A database of chemical properties within the Risk Assessment Information System (RAIS) (<http://risk.lsd.ornl.gov/>) was used to obtain values of K_{ow} for BaP and DDE of 1.0 E6 and 3.24 E6 , respectively. The K_d for organic chemicals is usually the product of K_{oc} and f_{oc} when total solids are used to partition, but in the case of the ICM model, inorganic suspended solids (ISS) and suspended POC are used for inorganic and organic contaminants, respectively, thus, care must be taken in defining K_d for use in ICM as explained below. The POC concentration is the product of f_{oc} and TSS for the water column and the product of f_{oc} and sediment bulk density for the sediment bed.

Since K_d is an important parameter that can be affected by ambient conditions and can vary from system to system for the same chemical, testing was conducted with the RECOVERY model (Ruiz and Gerald, 2001; Boyer et al., 1994) to validate the selected values for K_d and K_{ow} . RECOVERY is a time-varying model that treats the water column as a single, fully mixed cell of known area, depth, and flushing rate and represents the bottom sediments as a series of layers over the vertical dimension. Thus, this model, like the lake model, produces time-varying concentrations for the water column and bottom sediments. The model assumes a constant flushing rate or flow through the system. RECOVERY was run to quasi-steady-state assuming no settling, resuspension, degradation, volatilization, or flushing (i.e., a large volume with very small through-flow, thus, a very large residence time); only equilibrium sediment–water partitioning was included. Sediment concentrations measured from the floodwaters were input to the model, and overlying equilibrium water concentrations were computed by the

model and compared with measured water values taken concurrent with the sediment measurements in the floodwaters. The model indicated that the value of 4000 L/kg for lead K_d was representative of conditions in the New Orleans floodwaters. However, the value of K_d for arsenic had to be adjusted slightly to 500 L/kg to match observed water concentration. The K_{ow} for BaP and DDE also had to be decreased to 0.5 E6 and 1.0 E6 L/kg, respectively, to match observations. Since Eq. (1) is programmed into the RECOVERY model code, and f_{oc} is a measured input variable, it was easier and more rational to adjust K_{ow} for BaP and DDE. More than likely, adsorption to dissolved organic carbon (DOC), which is manifested as partitioning to water since DOC sorption is not included in the model, is the reason that K_{ow} had to be decreased to match observations. In reality, K_{ow} is a chemical property that should not require adjustment if DOC partitioning is included. These tests with RECOVERY resulted in relatively minor model adjustments that gave increased confidence in the modeled sorption process.

3.2. Hydrodynamic model boundary conditions

The hydrodynamic model was started with quiescent conditions on September 1, 2005, and run for 90 days applying boundary conditions for winds, water levels at the Rigolets Inlet, and pumped discharges from New Orleans. Wind velocities were based on observations from the New Orleans International Airport. However, wind data were not available until September 7 due to Katrina, so the winds applied to the model between September 1 and 7 were linearly ramped from 0.0 to the values observed on September 7. Thus, the period between September 1 and 7 were considered a model spin-up period and were not be used for model analysis and comparisons.

The water level boundary condition at the Rigolets Inlet included both meteorological and astronomical tide. For the astronomical tide, hourly predictions from NOAA at Waveland (station number 8747766) were used. There is a predicted tide station at Long Point, LA, in Lake Borgne, which is closer to the Rigolets entrance, but only high and low tides are available for that location. Measured water levels were available for the Waveland gage prior to Hurricane Katrina, but the gage was destroyed during the hurricane. Thus, predicted hourly tides at Waveland were used. The sub-tidal signal was obtained from water level recordings at East Bank 1 gage, Norco, Bayou LaBranche, LA (gage number 8762372) by using a 48-h moving average to filter out higher frequency signals. The sub-tidal signal was moved forward by 24 h and added to the astronomical tidal signal for Waveland to form the boundary condition at the Rigolets Inlet.

The pumped discharges and loadings to the lake were separated into Orleans Metro and Orleans East. Orleans Metro includes all the pump stations in Orleans Parish that are west of the IHNC and that pump water into the lake or into canals that empty into the lake, whereas, Orleans East

includes all the pump stations in Orleans Parish east of the IHNC that pump into the lake. Records indicate that Jefferson Parish pumps that discharge into the lake were not operated. Fig. 2 shows time-series plots of the combined, estimated pumping rates into the lake for Orleans Metro and Orleans East following Katrina (*actual* conditions). The flows for each pump station have been combined for the two areas for presentation, but the flow for each pump constituted a separate time series of discharge input for the model. The pump stations included in the model are shown in Fig. 3 with the exception of two temporary pumps in Orleans East that pumped into the lake. Since the lake model grid did not include canals that are connected to the lake, the discharges of any pump stations that are not located on the shoreline were assumed to be located at the confluence of the lake and the canal they pump into. Pumped discharges were used for inflows to the hydrodynamic model and for calculating loading inputs for the water quality model. The combined, time-integrated pumped flows of Fig. 2 represent a pumped volume of 0.54 E9 m³, which is approximately 5–10% of the lake volume.

As discussed in the Section 2, rainfall and pump capacities were used to establish the *baseline* pumping conditions. The rainfall reported at Slidell, LA, was approximately 20 cm for Katrina; other gages in the area did not report. The rainfall reported at the New Orleans International Airport for Rita was 5.84 cm. Given the approximate, combined collection basin area for Orleans Metro and Orleans East of 2.8 E8 m², the rainfall volumes for Katrina and Rita were about 5.7 E7 and 1.7 E7 m³, respectively, or roughly 1/10 of the actual pumped volumes. With the Orleans Parish pump-to-lake total discharge capacity of approximately 1076 m³/s, rainwater could have been pumped out in less than a day following each hurricane. Of course, this pumping period assumes no overtopping of the levees. The pump-out time for Katrina under these assumptions is about 0.6 days. The capacity of

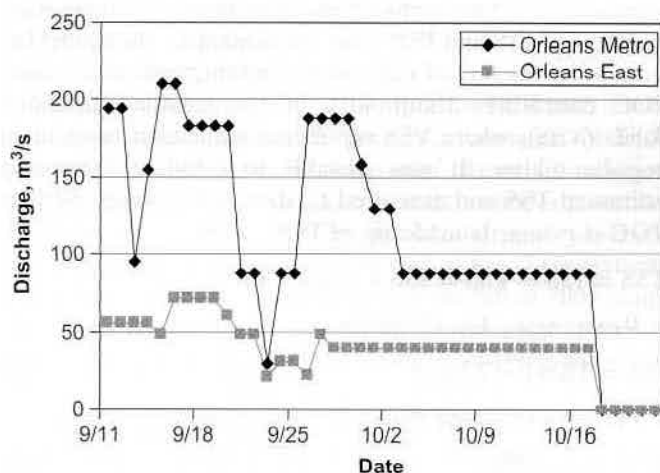


Fig. 2. Time series of combined *actual* pump discharges for Orleans Metro and Orleans East that were introduced into the lake.

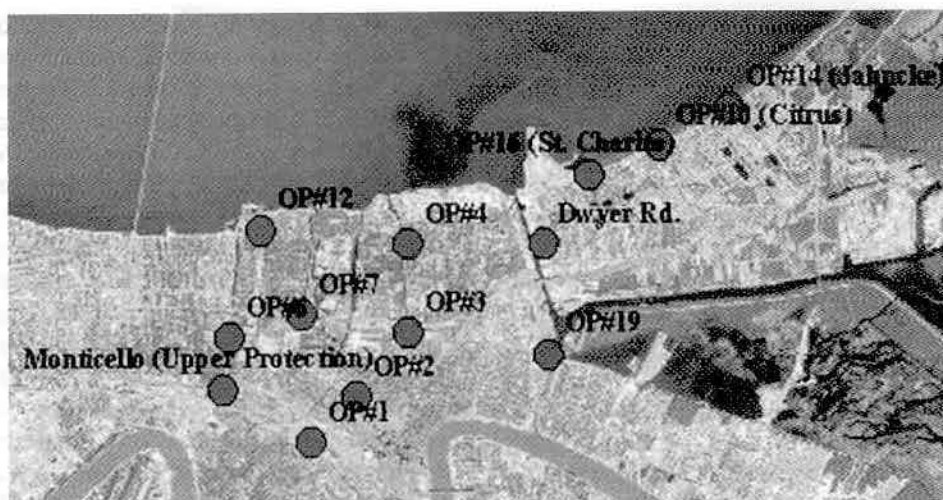


Fig. 3. Locations of pump stations for Orleans Parish included in the model that pumps into the lake.

each pump is known, and it was assumed that each pump would have been run at capacity for the *baseline* condition. Examination of pump records during tropical storm Isadora in September 2002 indicated this was a reasonable assumption. However, the model can accept only daily inputs for flows and loads (i.e., flow and load is assumed constant over each day, but can change from day to day). Therefore, the pump capacities were adjusted to provide a daily flow equal to the amount of rainwater to be emptied. For example, if a pump capacity is $100 \text{ m}^3/\text{s}$, then the flow used for the model pump was $60 \text{ m}^3/\text{s}$ based on the Katrina pump-out time of 0.6 days.

3.3. Water quality model inputs

The ICM model includes ISS and suspended POC as modeled state variables, rather than TSS. The current version of the model allows simulation of one inorganic contaminant that sorbs to ISS and one organic contaminant that sorbs to POC. As discussed earlier, TSS was estimated based on turbidity measurements, but there were no data for ISS and POC that are needed by the model for simulating the fate of particulate contaminants in the lake. POC constitutes about 40% of the volatile suspended solids (VSS), where VSS represents suspended particulate organic matter. It was possible to estimate ISS using estimated TSS and measured f_{oc} data and recognizing that TOC is primarily made up of POC, thus

$$\text{TSS} = \text{ISS} + \text{VSS} = \text{ISS} + 2.5f_{oc}\text{TSS}. \quad (2)$$

Rearranging Eq. (2) yields

$$\text{ISS} = \text{TSS}(1 - 2.5f_{oc}). \quad (3)$$

POC is calculated from

$$\text{POC} = f_{oc}\text{TSS}. \quad (4)$$

Concentrations of ISS and POC were held constant as background values throughout the lake by setting the

initial conditions and all boundary conditions to the same constant values.

The fraction of particulate inorganic contaminant concentration to total inorganic contaminant concentration can be determined through reversible equilibrium partitioning from

$$F_{pi} = \frac{K_d \text{ISS}}{1 + K_d \text{ISS}}. \quad (5)$$

Likewise, the fraction of particulate organic contaminant concentration to total organic contaminant concentration can be determined from

$$F_{po} = \frac{K_d \text{POC}}{1 + K_d \text{POC}}. \quad (6)$$

The units for K_d in ICM are m^3/g , thus, the values presented previously were converted from L/kg to m^3/g by multiplying by $1.0 \text{ E-}6$. The K_d values input for lead (Pb) and arsenic (As) were $0.5 \text{ E-}3$ and $4.0 \text{ E-}3 \text{ m}^3/\text{g}$, respectively. For ICM, K_d and K_{oc} are operationally the same since f_{oc} is taken into account by using POC instead of TSS to compute F_{po} . Thus, the K_d values for BaP and DDE (after applying Eq. (1) to get K_{oc}) used in ICM were 0.3 and $0.6 \text{ m}^3/\text{g}$, respectively.

The ICM model requires input of the volatilization rate (K_{vol} , m/day) rather than computing it from chemical properties, wind, and hydrodynamic flow conditions. Wind is the predominant forcing rather than flow for volatilization in lakes, thus, volatilization rate was computed based on wind speed. Using a wind speed of 5 miles per hour (3 m/s), Henry's law constants for BaP and DDE of $4.5 \text{ E-}7$ and $4.0 \text{ E-}5 \text{ atm m}^3/\text{mole}$, respectively, and respective molecular weights of 252 and 318 g/mole , K_{vol} was computed using the algorithm within the RECOVERY model. Volatilization within RECOVERY is based on the Whitman two-film theory as described by Chapra (1977), where the gas and liquid side mass transfer rates are computed from wind speed and molecular weight based

upon relationships presented by Mills et al. (1982). The resulting values of K_{vol} computed for BaP and DDE were 0.005 and 0.19 m/day, respectively. The ICM model multiplies K_{vol} by the dissolved organic chemical concentration in the surface layer of the water column to calculate the volatilization flux ($\text{g}/\text{m}^2/\text{day}$). The dissolved organic chemical concentration is the product of the total organic chemical concentration and the quantity $(1-F_{po})$.

Turbidity measurements for Lake Pontchartrain are routinely measured. Lake turbidity values obtained during the fall of 2005 following Katrina were analyzed over time and for all recording stations to obtain a lake-wide median value of 8.2 nephelometric turbidity units (NTU) (LPBF, 2006; Pardue et al., 2006). The lake median turbidity was converted to a median TSS value of 19.2 mg/L for use in the lake model for background suspended sediment. Benthic sediment resuspension rate was set to zero, and the burial rate was set to 0.026 m/yr in the model; the surficial sediment bed layer thickness was set to 0.2 m. Degradation rates were set to zero for all constituents except FCB.

The concentrations used to establish the lake water quality model loadings are shown in Table 1. The loading concentrations were categorized by median and 95UCL, which were determined from statistical analysis of all the post-Katrina floodwater measurements taken in the two areas (Orleans Metro and Orleans East) using the database compiled as described earlier. For some cases, the median and 95UCL are the same due to lack of variability in the measured concentrations. Loading concentrations for *baseline* conditions were set equal to those for *actual* conditions.

4. Calibration/validation

Given the observational data limitations, it was not possible to calibrate and validate the lake hydrodynamic

and water quality models to the extent normally desired. The flow fields and transport computed with these models have been found to be quite accurate in other studies if sufficient boundary conditions for inflows, water levels, winds, and constituent loadings are provided. A limited level of model calibration/validation was undertaken using water surface elevations and FCB concentrations measured during the later summer/fall of 2005. The hydrodynamic model was executed for *actual* conditions following Katrina so the model could be calibrated against observed water surface elevations in the lake. The water quality model was applied for FCB during *actual* conditions following Katrina to validate the model against observed FCB in the lake using the calibrated hydrodynamic model output.

The computed and observed water surface elevations during September and early October 2005 at the Norco gage of Lake Pontchartrain are shown in Fig. 4. This was the only water level observation gage available in Lake Pontchartrain for model comparison, and this gage was not reported between October 10 and December 2, 2005. The model compares closely with the observations throughout the observation period with the exception of the first 4 days, which was the model spin-up period when the model was started with quiescent conditions at mean sea-level elevation. The large spike in water level around September 24 was due to Hurricane Rita. The model performs exceptionally well given that the boundary conditions at the open sea boundary were synthesized from the combination of predicted astronomical tides and filtered sub-tidal meteorological forcing. Measured water levels at the seaward boundary are often available for estuarine and coastal hydrodynamic model applications. It was not necessary to make any adjustments in model parameters, such as bottom roughness and wind drag coefficient.

Pumped flows were a dominant factor in the lake currents under the *actual* conditions as can be seen in Fig. 5, which shows the surface layer velocity vectors computed for September 12, 2005, near the end of the day. Animation of the currents showed that the speeds increase and decrease dramatically near the south shore when pumping begins and ends.

The lake water quality model output for FCB with *actual* conditions was compared to lake measurements of FCB obtained by the Lake Pontchartrain Basin Foundation (LPBF, 2006). The Foundation's water sampling station locations are shown in Fig. 6. Model and observed concentrations versus time are plotted in Fig. 7 for stations 1–4 where data were available during the fall of 2005 along the south shore. Data for station 5 were not available during those months, and data at stations along the north shore were not included since the model did not include any FCB loadings from the north shore.

The observed data in Fig. 7 are less than ideal. There are no observations for September when the highest loadings and greatest computed concentrations occur. Model loadings end on October 18 when pump-out was

Table 1
Lake loading concentrations (total) by region for *baseline* and *actual* conditions.

Constituent	Median ($\mu\text{g}/\text{L}$)	95UCL ($\mu\text{g}/\text{L}$)
<i>Orleans Metro</i>		
Arsenic	20	20
BaP	5	5
DDE	0.05	0.05
Lead	5	44
Fecal coliform bacteria	2200 ^a	70,041 ^a
<i>Orleans East</i>		
Arsenic	20	26
BaP	5	5
DDE	0.05	0.38
Lead	2.5	12
Fecal coliform bacteria	200 ^a	32,869 ^a

^aUnits are cfu/100 mL or MPN/100 mL.

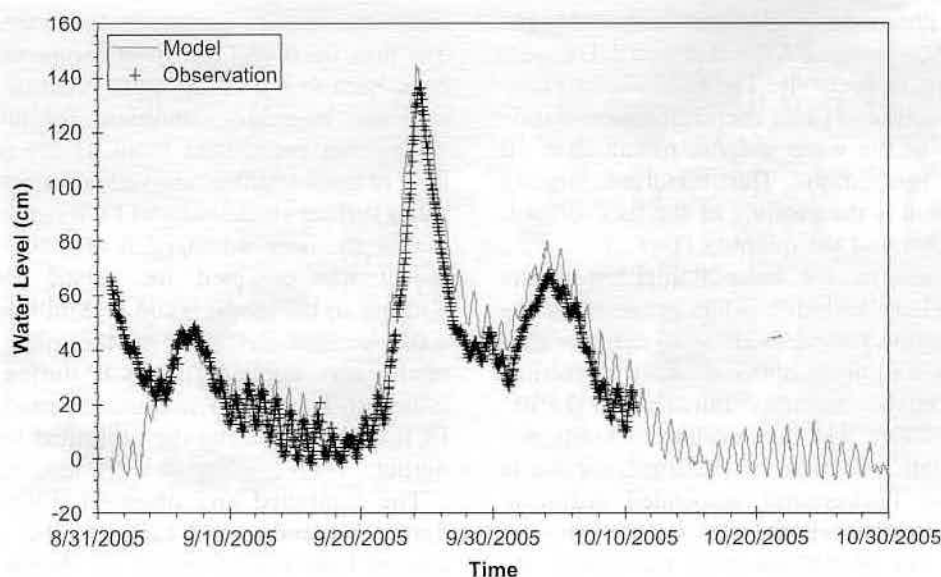


Fig. 4. Computed and observed water level in Lake Pontchartrain for tide gage 8762372 East Bank I, Norco, Bayou LaBranche, LA.

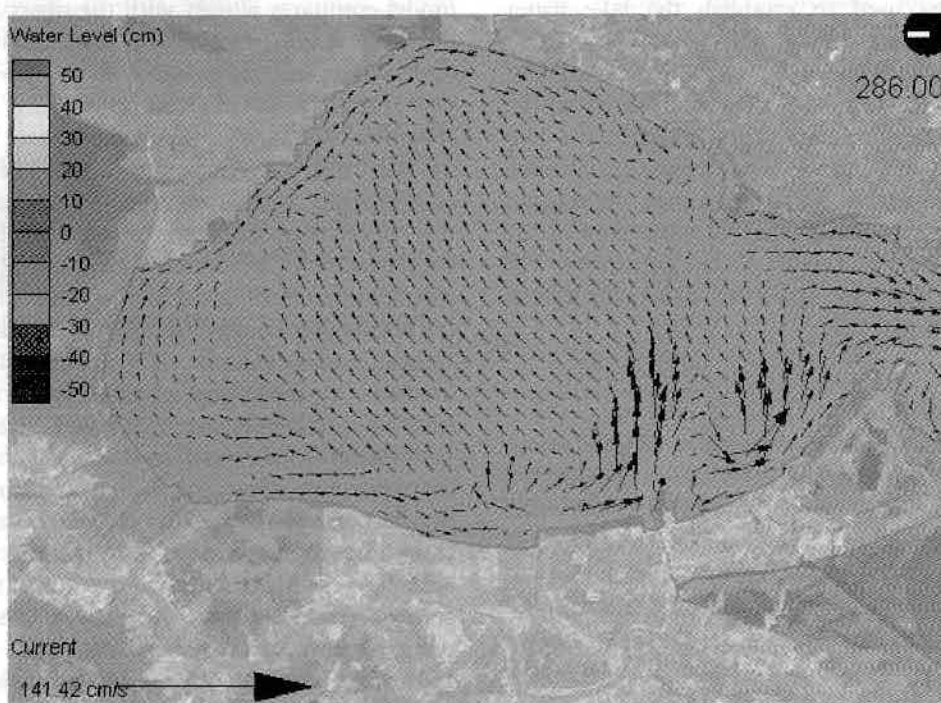


Fig. 5. Computed surface layer currents at the end of September 12, 2005, *actual* conditions.

completed, but observations indicate that there must have been other source loadings into the lake after that date that were not accounted for in the model. Thus, there is a window of only about 18 days in early October with which to meaningfully compare model and observations. During that window, the model can be compared with the observations. Comparisons after October 18 should be disregarded since there are no model loadings after that date. There is not enough information in Fig. 7 to evaluate model validation. It should be noted that the model loading concentration was constant over time and equal to

the median concentrations in the floodwaters, whereas the actual loading concentrations probably varied due to variations in pumped floodwater concentration over time and space.

The USGS collected lake sediment samples near the south shore and the causeway during September and October 2005 that were analyzed for a host of constituents (Demas, 2006¹), including those modeled. Measured BaP

¹Demas, C.R., 2006. Personal communication. US Geological Survey Louisiana Water Science Center, Baton Rouge, LA.

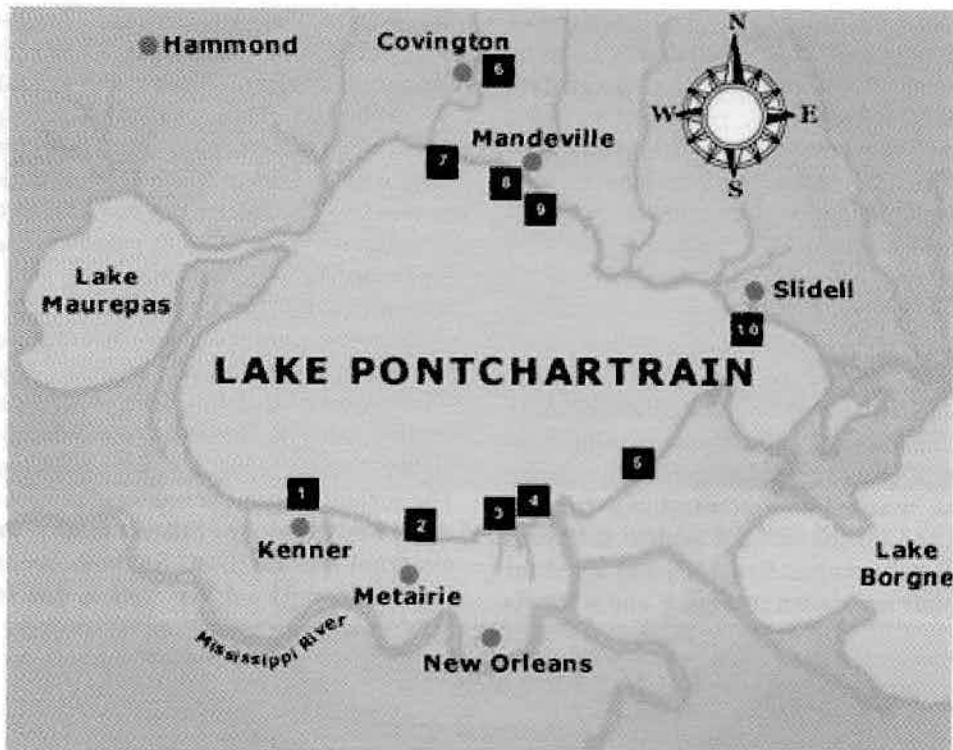


Fig. 6. Lake Pontchartrain Basin Foundation water quality sampling station locations (from Lake Pontchartrain Basin Foundation, http://www.saveourlake.org/water_quality.asp).

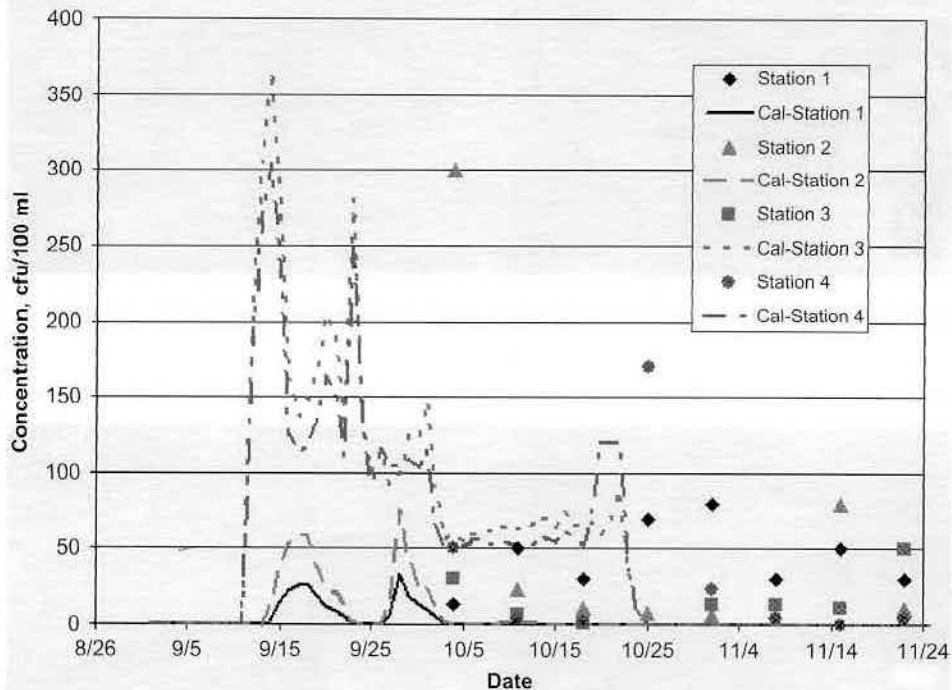


Fig. 7. Model-computed (Cal-Station and solid lines) FCB concentrations for *actual* conditions and median loading concentration and measured (symbols) FCB concentrations following Katrina at four stations along the south shore of Lake Pontchartrain.

ranged between 17 and 290 $\mu\text{g}/\text{kg}$, where model computations for sediment BaP with *actual* conditions were approximately 40 $\mu\text{g}/\text{kg}$ in the sampled area of the lake. The fact that the model result falls within the range of

observations for this chemical increases the level of confidence in the model. Computed sediment concentrations for DDE were also about the same order of magnitude as those measured. However, computed

sediment concentrations for As and Pb were two-orders of magnitude less than measured. This result is not surprising since only two loading events (Katrina and Rita) were included in the model. The prototype sediments have experienced many loading events over the years, and metals do not degrade; thus, the sediments can have a long memory for metal contaminant loading events.

5. Scenario results

5.1. Comparison of actual versus baseline conditions

The lake water quality model was executed for both scenarios (*baseline* and *actual* hydrodynamic conditions and loadings) using median and 95UCL loading concentrations. Computed maximum concentrations for the model surface layer and for the surficial benthic sediments were determined for each computational cell and saved for plotting. Example plots are shown in Figs. 8 and 9 for As

for both *actual* and *baseline* conditions, respectively. In general, the outermost extent of the maximum concentration contours for *actual* conditions extend further out from the shore and cover a larger area, whereas the *baseline* contours are more compact. Also, the outermost contours have higher concentrations for the *actual* conditions. The greater spread is due to the longer duration of pumping and the overall greater total mass loading of the *actual* conditions associated with the larger water volumes pumped. However, the pump discharge rates of the *baseline* conditions are near pump capacity, which results in a larger flow rate and mass loading rate, but for a much shorter duration. The short-term bursts of higher loading rates of the *baseline* conditions result in slightly higher overall maximum concentrations near the shore. The highest maximum sediment concentrations tend to be concentrated along the southeast shore of the lake, out from Orleans East, for both conditions as shown in Figs. 10 and 11 for As. This is due to the proximity to

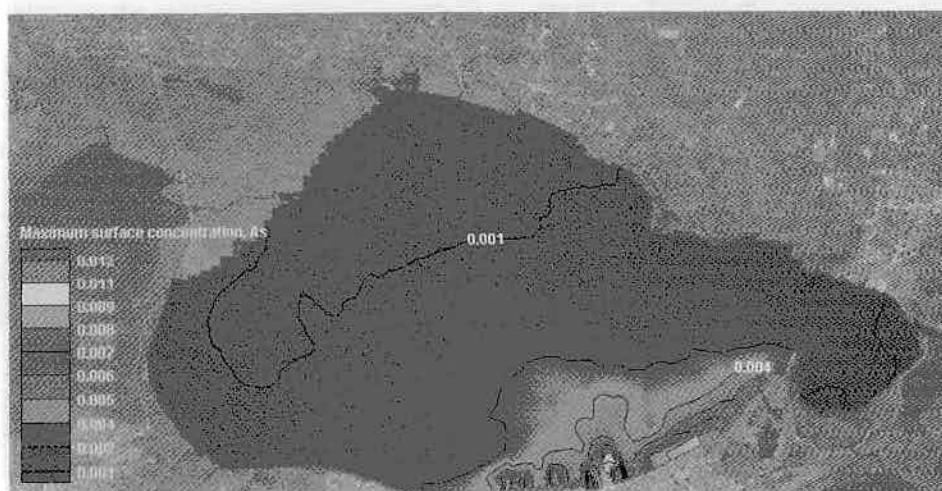


Fig. 8. Computed incremental maximum As water surface concentrations (mg/L total) in Lake Pontchartrain for *actual* conditions, median loading concentrations.



Fig. 9. Computed incremental maximum As water surface concentrations (mg/L total) in Lake Pontchartrain for *baseline* conditions, median loading concentrations.

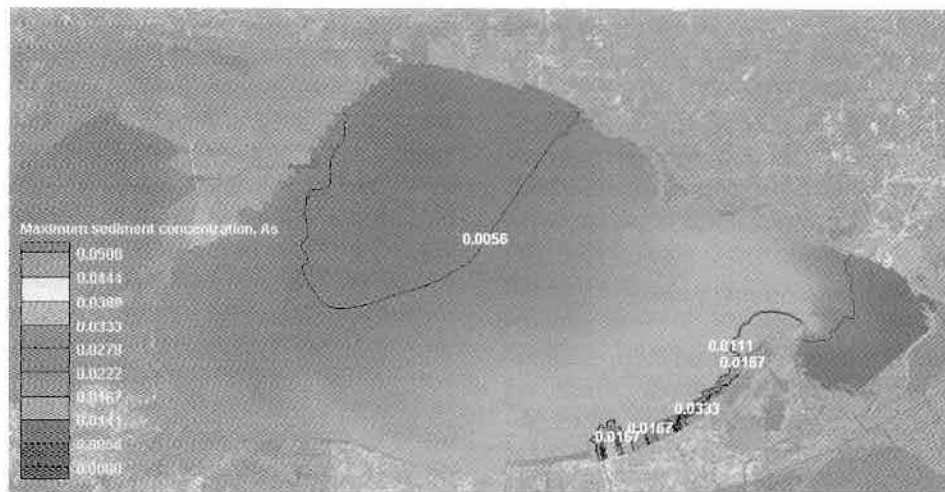


Fig. 10. Computed incremental maximum As sediment concentrations (mg/kg total) in Lake Pontchartrain for *actual* conditions, median loading concentrations.

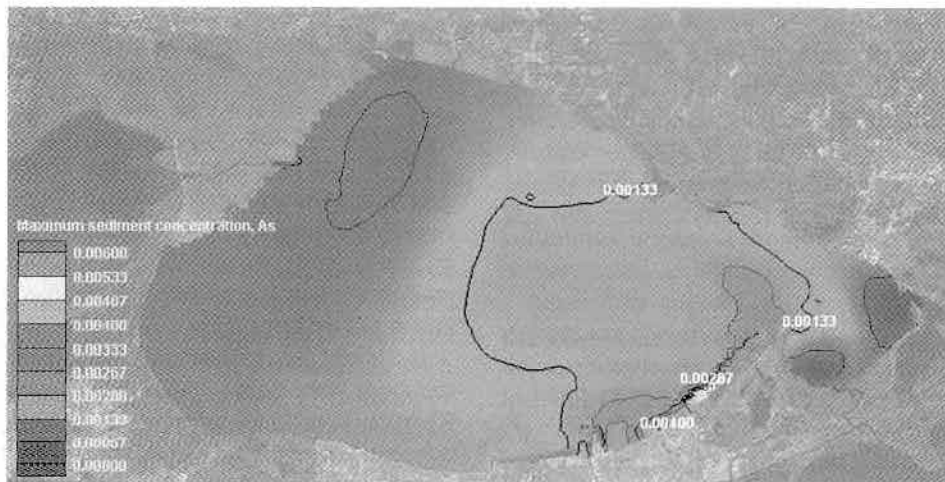


Fig. 11. Computed incremental maximum As sediment concentrations (mg/kg total) in Lake Pontchartrain for *baseline* conditions, median loading concentrations.

Table 2

Computed maximum water ($\mu\text{g/L}$) and sediment (mg/kg) concentrations (total) for Lake Pontchartrain for *actual* and *baseline* conditions and median and 95UCL loading concentrations

Condition	As water	As sediment	BaP water	BaP sediment	DDE water	DDE sediment	Pb water	Pb sediment	FCB water ^a
Actual	13	0.048	3.7	0.173	0.036	0.0024	3.7	0.053	1055
Actual95	16	0.066	3.7	0.173	0.209	0.0171	25.4	0.384	42,214
Base	14	0.0052	3.7	0.014	0.037	0.000172	3.7	0.0062	1413
Base95	14	0.0054	3.7	0.014	0.053	0.000598	32.1	0.051	44,780

Note: Actual and Base are median loading concentrations, and Actual95 and Base95 are 95UCL loading concentrations.

^aUnits for FCB are cfu/100 mL or MPN/100 mL.

pump discharges, the current conditions, and the shallow water in this area.

The results in Table 2 are computed incremental, maximum sediment and water concentrations. The term incremental is inserted because the water quality model was run with initial water and sediment concentrations set to

zero; thus, results reflect the incremental change above a pre-existing condition, such as pre-Katrina concentrations. It is apparent from Table 2 that the maximum water concentrations for the *actual* conditions are about the same or a little less than those for the *baseline* conditions due to the higher flow rates of the *baseline* conditions (more

pumps operating near capacity) which results in less time for settling of particulate matter and die-off for FCB. However, the maximum change in sediment concentrations for the *baseline* condition are roughly an order of magnitude less than those of the corresponding *actual* condition for all constituents, which is due to the much lower mass loading for the *baseline* condition.

5.2. Comparisons to ecological screening values

Dissolved water concentrations were needed for comparison to water quality criteria and standards, which are stated as dissolved. Dissolved concentrations were obtained by multiplying the fraction of dissolved to total contaminant concentrations in the water column (F_{dw}) times the maximum total concentrations in water in Table 2. The dissolved concentrations are reported in Table 3 for each constituent along with the dissolved fractions.

Computed maximum dissolved water column concentrations and maximum sediment concentrations were compared with ecological water and sediment quality screening values in Table 4. US Environmental Protection Agency (US EPA, 1986) recommends primary contact protective limits for FCB of 400 MPN/100 mL for a single sample. The computed maximum water concentrations for As and BaP were less than the EPA water quality criteria and LA

water quality standards for both conditions and both loading concentrations. The computed maximum water column concentrations for Pb exceeded EPA and LA water quality standards for both conditions with the 95UCL loading concentrations, and the concentrations for DDE exceeded the LA criteria for the *actual* conditions with 95UCL loading concentrations. Maximum concentrations for FCB in water exceeded EPA criteria for both conditions and both loading concentrations, but FCB exceedence in the lake frequently occurs during dewatering of New Orleans storm water (Jin et al., 2004).

The computed maximum sediment concentrations for As and Pb were less than the sediment quality guideline values for both conditions and both loading concentrations. The computed maximum sediment concentrations for BaP and DDE were less than the sediment screening criteria for both loading concentrations of the *baseline* conditions, but sediment concentrations for both constituents exceeded the guideline values for both loading concentrations under the *actual* conditions.

6. Discussion

Considering the uncertainties in the loading concentrations for *actual* and *baseline* conditions, one cannot conclude that dewatering will definitely result in specific concentrations or criteria exceedence. Model results should be viewed as relative, not absolute. One of the strengths of models rests in the ability to examine incremental changes and make relative comparisons.

It should be recognized that incremental increases in sediment concentration for some constituents due to the Katrina–Rita loading events may be miniscule relative to concentrations already in the prototype sediments resulting from years of accumulation from previous events. The increase in lake sediment metal concentrations computed by the model for *actual* conditions are very small compared with pre-Katrina concentrations. Pre-Katrina mean sediment concentrations reported by Penland et al. (2002) were 7.02 parts per million (ppm) and 17.5 ppm for As and Pb, respectively; thus, the maximum increase in sediment concentrations above pre-Katrina (background) values computed by the model for *actual* conditions and median loading concentrations was 0.7% for As and 0.3% for Pb. Limited sampling near the south shore of the lake following Katrina revealed that sediment concentrations for As and Pb were about the same as pre-Katrina values, with As values of 3–11 ppm and Pb values of 12–33 ppm (Demas, 2006; see footnote 1), thus, confirming the model that showed dewatering of New Orleans following Hurricanes Katrina and Rita had little impact on lake sediment concentrations of metals. Pre-Katrina sediment concentrations for BaP and DDE were not found, but post-Katrina concentrations of 17–290 ppb for BaP and non-detection—5.3 ppb for DDE were measured (Demas, 2006; see footnote 1). Sediment concentrations computed by the model for *actual* conditions and median loading concen-

Table 3

Dissolved fractions in the water column (F_{dw}) for each constituent and computed maximum water ($\mu\text{g/L}$) concentrations (dissolved) for *actual* and *baseline* conditions and median and 95UCL loading concentrations.

Condition	As	BaP	DDE	Pb
F_{dw}	0.99	0.89	0.80	0.93
Actual	12.9	3.3	0.029	3.4
Actual95	15.8	3.3	0.167	23.6
Base	13.9	3.3	0.030	3.4
Base95	13.9	3.3	0.042	29.8

Table 4

Screening-level ecologically protective benchmarks

Criteria	As	BaP	DDE	Pb
EPA, water ($\mu\text{g/L}$ dissolved)	36 ^a	300 ^b	14 ^c	8.1 ^a
LA, water ($\mu\text{g/L}$ dissolved) ^d	36 ^d	NA	0.14 ^d	4.0 ^e
Sediment (mg/kg dry) ^f	7.24	0.0888	0.00207	30.2

^aChronic EPA Water Quality Criteria (US EPA, 2002).

^bMarine lowest observable effects level (NOAA, 1999).

^cAcute EPA Water Quality Criteria (US EPA, 2002).

^dChronic LA Water Quality Standards (LADEQ, 2000).

^eChronic LA Water Quality Standard for lead hardness adjusted (120 ppm CaCO_3) (LADEQ, 2000).

^fMarine threshold effects limit (TEL) from MacDonald et al. (1996) for coastal and marine waters in the Gulf of Mexico.

trations in the same vicinity as those measured were 40 ppb for BaP and 0.3 ppb for DDE. The increase in sediment concentration computed by the model for BaP is within the range of measured sediment concentrations, rather than much less as for the metals, which is reasonable given that pre-Katrina BaP sediment concentrations may have been relatively low due to the degradation and volatilization potentials of this compound. DDE would tend to persist in the sediments longer than BaP but not as long as the metals; thus, the percentage of computed sediment concentration increase to measured post-Katrina concentration of DDE seems reasonable as compared with the results for BaP and the metals.

The assumption was made for the modeling that storm water and floodwater concentrations were the same under *baseline* and *actual* conditions. Any efforts to improve the model should focus on obtaining water quality measurements in storm water under normal, *baseline* conditions without flooding through or over the levees.

At one point, consideration was given to trying to estimate the source terms that resulted in the floodwater contamination. Models are much more robust if the source terms can be quantified. However, such an undertaking would have required a tremendous effort with very high uncertainty of the results. Therefore, this idea was dropped from further consideration and is most likely not a viable goal for future studies. Furthermore, Mielke et al. (2004) reported high soil concentrations of polynuclear aromatic hydrocarbons (PAH) and metals in urban New Orleans, especially near busy city streets. These data are pre-Katrina and represent a common condition in urban areas with heavy traffic. Thus, a substantial portion of floodwater contamination may have been caused by flooding of already contaminated soils rather than rupturing or leaking chemical storage tanks. Flooding and the subsequent dewatering resulted in exposing the environment surrounding New Orleans to these contaminants. However, such exposure most likely occurs even during normal (*baseline*) dewatering, but to a less degree due to less storm water and shorter pumping durations.

7. Conclusions

The Lake Pontchartrain model indicated that incremental increases in lake sediment concentrations of contaminants as a result of the *actual* dewatering event were about an order of magnitude greater than for *baseline* removal of storm water without levee failure and overtopping. However, increases in concentration of As, Pb, and DDE in sediment were small relative to measured and suspected pre-Katrina sediment concentrations for these constituents, whereas the increases in sediment concentrations of BaP were about the same order of magnitude of post-Katrina measurements. Thus, dewatering of floodwaters is expected to have a negligible to minor impact on lake sediments relative to background concentrations for metals and long-life organic compounds; but a measurable impact is

expected for more rapidly degrading compounds, such as PAHs. Model-computed maximum sediment concentrations for BaP and DDE exceeded ecologically protective sediment quality guideline values for *actual* conditions, whereas concentrations of these chemicals did not exceed these screening values for *baseline* conditions. However, the sediment areas that exceeded sediment quality criteria are relatively small areas close to the southeast shore. Exceedence of guidelines should be interpreted with caution because the intended use of sediment quality guideline values is to screen sediments for potential adverse effects on benthic invertebrate organisms, not to quantify risk or an impact (Wenning et al., 2005).

Elevated concentrations of FCB in water are expected to occur, and do occur (Jin et al., 2004), in the lake during dewatering regardless of levee conditions (i.e., levee failures/overtopping or not). In fact, water concentrations of all constituents should be about the same, or even less, with levee failures since fewer pumps may be operating and may be operating below capacity. Lower pump discharge rates result in lower water concentrations due to larger residence times in ambient waters with greater opportunity for settling and dilution. The reason that incremental increases in sediment concentrations are expected to be higher with levee failures is that more floodwater volume must be removed, thus, dewatering takes longer and more contaminant mass is discharged to receiving waters, which is manifested as higher sediment concentrations.

Lead may present water quality concerns under any dewatering conditions regardless of the levee failures/overtopping or not. Computed maximum water concentrations of Pb exceeded water quality criteria for both *actual* and *baseline* conditions when loading concentrations are high (i.e., 95UCL). However, elevated concentrations of metals and PAHs existed in urban New Orleans soils before Katrina. Thus, the presence of these constituents is expected for urban storm water and in the pumped effluents, with or without levee failures.

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Price-based vs. quantity-based environmental regulation under Knightian uncertainty: An info-gap robust satisficing perspective

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Abstract

Conventional wisdom among environmental economists is that the relative slopes of the marginal social benefit and marginal social cost functions determine whether a price-based or quantity-based environmental regulation leads to higher expected social welfare. We revisit the choice between price-based vs. quantity-based environmental regulation under Knightian uncertainty; that is, when uncertainty cannot be modeled with known moments of probability distributions. Under these circumstances, the policy objective cannot be to maximize the expected net benefits of emissions control. Instead, we evaluate an emissions tax and an aggregate abatement standard in terms of maximizing the range of uncertainty under which the welfare loss from error in the estimates of the marginal benefits and costs of emissions control can be limited. The main result of our work is that the same criterion involving the relative slopes of the marginal benefit and cost functions determines whether price-based or quantity-based control is more robust to unstructured uncertainty. Hence, not only does the relative slopes criterion lead to the policy that maximizes the expected net benefits of control under structured uncertainty, it also leads to the policy that maximizes robustness to unstructured uncertainty.

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1. Introduction

Environmental regulations are chosen in a world in which authorities have only imperfect information about the underlying benefits and costs of environmental control. In his seminal paper, Weitzman (1974) provides guidance for the optimal choice between price-based and quantity-based emissions control (i.e., an emissions tax vs. a competitive market for transferable emissions quotas) that has become conventional wisdom among environmental policy scholars and practitioners. Weitzman (1974) shows that when the marginal benefits and marginal costs of emissions control are linear (at least to a local approximation), when authorities are uncertain about the intercepts of these functions (but not their slopes), and when the benefits and costs of emissions control are uncorrelated,

then a price-based regulation is more efficient than a quantity-based regulation if the slope of the marginal cost function is steeper than the absolute value of the slope of the marginal benefit function, and a quantity-based regulation dominates in the opposite case. This decision criterion is determined from a comparison of expected social welfare (expected benefit minus cost) under the two types of regulations.¹

¹Weitzman (1974) demonstrates that this decision criterion must be modified when benefits and costs are correlated. See Stavins (1996) for a further exposition of this case. Weitzman, Laffont (1977), and Malcomson (1978) examine modifications to the relative-slopes criterion when these are also uncertain. Linearity to a local approximation of the marginal benefit and marginal cost functions is also important for the determination of the prices vs. quantities criterion. Malcomson (1978) and Weitzman (1978) reexamine Weitzman's original work when local linear approximations to the benefit and cost function are not appropriate. In our paper, we stick to linear marginal benefit and cost functions with uncorrelated uncertainty in their intercepts, because it is this problem that drives the conventional wisdom of environmental economists about the choice between emissions taxes and aggregate abatement standards (Baumol and

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Weitzman, as well as the small army of scholars who have contributed to the prices vs. quantities debate since 1974, assumed that uncertainty about the marginal benefit and cost functions could be characterized by known moments of probability distribution functions (i.e., means and variances) over the errors in estimates of the marginal benefit and cost functions.² Indeed, the criterion for choosing between price-based and quantity-based regulations is determined from a comparison of expected social welfare under the two regulatory instruments. While it has proven useful to assume that the error structures of estimates of the marginal benefit and cost functions are known, in many cases if not most, environmental authorities must design control policies even when they are not confident of the error structures.³ That is, the world of environmental decision making may be usefully characterized by Knightian uncertainty in which, not only are the benefit and cost functions unknown, but the distributions of the estimates of these functions are also unknown.⁴

In this paper, we revisit the price vs. quantity debate from the perspective of robust satisficing when the errors in the estimates of the benefits and costs of emissions control are completely unstructured. Info-gap decision theory (Ben-Haim, 2006) provides a useful way to think about the regulatory choice of emissions control instruments in the face of true Knightian uncertainty.⁵ The heart of info-

gap analysis is the pursuit of decisions that maximize the range of uncertainty about model parameters or functions within which the decision maker is certain to achieve a specified performance criterion. One decision is more robust than another if the range of uncertainty under which the performance criterion is met is larger.⁶ In our case, uncertainty is about the true values of the intercepts of the marginal benefits and costs of emissions control and the performance criterion is to hold the welfare loss associated with error in the estimates of these values to be no greater than some value. For a given loss associated with estimation error, one emissions control policy is more robust than another if the range of error in the estimates of the benefit and cost functions under which the performance criterion is met is larger. That is, we choose the control policy to satisfy the welfare loss and maximize the immunity to uncertainty in the intercepts of marginal benefits and costs.

Weitzman's (1974) initial formulation identifies disturbances to the cost and benefit functions which are "unobserved and unknown at the present time. While the determination of these disturbances could involve elements of genuine randomness, it is probably more appropriate to think primarily in terms of an information gap" (p. 480). In our work, we will refer to this info-gap perspective as "unstructured" uncertainty, identifying it with Knightian uncertainty (Knight, 1921) or, as Weitzman does, with Hayek's work.

Weitzman subsequently puts "more structure on the problem" (p. 483) in order to derive his main result (his Eq. (20)), which depends on the variance of marginal cost and on the validity of a second-order expansion of the cost and benefit functions. We will refer to this, and similar, moment-based approaches as "structured" uncertainty.

We apply info-gap analysis to the choice between price-based and quantity-based environmental regulation in the conventional model of environmental control under uncertainty. The main result of this paper is that the same criterion involving the relative slopes of the marginal benefit and cost functions that Weitzman derived in the case of structured uncertainty about the estimates of the benefit and cost functions also reveals whether price-based or quantity-based regulation is more robust to this uncertainty when it is completely unstructured. Although we come to the same decision criterion, our motivation for deriving this criterion is very different. While the decision criterion for choosing between price-based and quantity-

(footnote continued)

Oates, 1988). In fact, many recent contributions to this literature (e.g., Hoel and Karp, 2002; Moledina et al., 2003; Montero, 2002; Quirion, 2004) assume linear marginal benefit and cost functions with only intercept uncertainty. We note that the approach we take in this paper, that of robust satisficing, can be applied to all of the complicating factors mentioned in this footnote.

²Recent contributions to the prices vs. quantities debate in the area of environmental management include extensions to situations involving imperfectly enforced environmental regulations (Montero, 2002), strategic competition among regulated firms (Moledina et al., 2003), economies with pre-existing distortions from labor or capital taxes (Quirion, 2004), and dynamic environments induced by the control of stock pollutants (Hoel and Karp, 2002; Newell and Pizer, 2003), in particular the control of greenhouse gas emissions to mitigate global climate change (Pizer, 2002).

³For example, Philibert (2006) recognizes that the design of policies to control greenhouse gases suffers from "deep uncertainty" about future damage from climate change, because "... there is no scientific agreement on the probabilities of distribution of the various possible outcomes." (p. 9). Given the long time frame involved in the control of greenhouse gases, we would argue that this problem probably suffers from deep uncertainty about future abatement costs as well.

⁴Knight was concerned "with situations which are far too unique, generally speaking, for any sort of statistical tabulation to have any value for guidance. The conception of an objectively measurable probability or chance is simply inapplicable." This is what Knight called "true uncertainty" (Knight, 1921, pp. 231–232), and it dominates many economic policy decisions because local or firm-specific details and future contingencies are poorly understood by policy makers.

⁵Info-gap decision theory has been applied to a wide variety of problems, including financial risk assessment (Ben-Haim, 2005), search behavior in animal foraging models (Carmel and Ben-Haim, 2005), policy decisions in marine reserve design (Halpern et al., 2006), natural resource conservation decisions (Moilanen and Wintle, 2006), inspection decisions by port authorities to detect terrorist weapons (Moffitt et al., 2005) and

(footnote continued)

invasive species (Moffitt et al., 2007), technological fault diagnosis (Pierce et al., 2006) and engineering model-testing (Vinot et al., 2005).

⁶Info-gap robust satisficing is a quantitative combination of Knightian uncertainty with Simon's concept of bounded rationality. The robust-satisficing policy maker seeks a decision which satisfies the performance and is robust to uncertainty. Simon (1983) stresses the importance of satisficing—doing good enough; meeting critical requirements—when decisions must be made with deficient or erroneous information (i.e. Knightian uncertainty) and limited computational resources.

based emissions control maximizes the expected net social benefits of emissions control, we show that this decision criterion also leads to the choice of policy that is most robust to estimation error when authorities do not have reliable information about the probability structure of this error. Hence, we provide a further justification for the use of the relative-slopes criterion that is conventional wisdom among environmental economists—not only does this criterion lead to the policy that maximizes the expected net benefits of control under structured uncertainty, it also leads to the policy that maximizes robustness to unstructured uncertainty.

The rest of the paper proceeds as follows: in Section 2, we lay out the structure of the info-gap approach to choosing between a price-based and a quantity-based environmental regulation under true uncertainty. In Section 3, we calculate the robustness to uncertainty of each policy type. In Section 4, we derive the condition under which the price approach is more robust to uncertainty than the quantity approach, and vice versa, and discuss the policy significance of our findings. We conclude in Section 5.

2. Info-gap robust satisficing

2.1. Info-gap uncertainty about the benefits and costs of pollution control

Let q denote aggregate reduction (abatement) in the emissions of some pollutant. The aggregate benefits and costs of abatement take on the familiar quadratic forms. The benefit and costs functions are, respectively:

$$B(q) = bq - B''q^2/2, \quad (1)$$

$$C(q) = cq + C''q^2/2, \quad (2)$$

where b , c , B'' and C'' are all positive constants, restricted to guarantee that optimal abatement levels are strictly positive throughout.⁷ The social welfare function is simply the difference between the benefits and costs of abatement:

$$\begin{aligned} W(q) &= B(q) - C(q) \\ &= (b - c)q - (B'' + C'')q^2/2. \end{aligned} \quad (3)$$

We assume that the quadratic forms for the benefit and cost functions and the numerical values of B'' and C'' have been verified, but that the values of b and c are highly uncertain. Note that b and c are the intercepts of the marginal benefit and marginal cost functions, respectively. Thus, this set-up is consistent with most of the literature on the prices versus quantities debate, in which it is typical to

assume that the marginal benefit and cost functions are known except for uncertainty about their intercepts.

Assume that the environmental authority possesses estimates of the intercepts of the marginal benefit and cost functions, denoted $\tilde{b}$ and $\tilde{c}$, but the factors that modify these parameters are complex and poorly understood, so we face true Knightian uncertainty: no reliable probabilistic model is available for the size of the estimation errors. That is, we must deal with the uncertainty in the estimates of these parameters without knowledge of the probability distribution functions that underlie them. Instead, we describe the uncertainty in the estimates of b and c with a fractional-error info-gap model for uncertainty in $\tilde{b}$ and $\tilde{c}$, which is the following unbounded family of nested sets of the marginal functions:

$$\begin{aligned} U(\alpha, \tilde{b}, \tilde{c}) &= \left\{ B'(q) = b - B''q, \right. \\ C'(q) &= c + C''q : \left| \frac{b - \tilde{b}}{\tilde{b}} \right| \leq \alpha, \left| \frac{c - \tilde{c}}{\tilde{c}} \right| \leq \alpha \left. \right\}, \quad \alpha \geq 0. \end{aligned} \quad (4)$$

It is clear that α represents the unknown fractional error in the estimates of the intercepts of the marginal benefit and cost functions. When the horizon of uncertainty, α , is zero, then the true intercepts, b and c , precisely equal the estimated values, $\tilde{b}$ and $\tilde{c}$. The range of possible intercept values increases as the horizon of uncertainty increases. The horizon of uncertainty is unbounded, so there is no known worst case. These properties are characteristic of all info-gap models (Ben-Haim, 2006).

2.2. Robustness

Generally, info-gap robustness is the greatest level of uncertainty with which a decision maker is certain to meet a pre-determined performance criterion. In our case, we look for the robustnesses of an emissions tax and an aggregate abatement standard, and our performance criterion is to limit the welfare loss from error in estimating the marginal benefit and cost functions. The emissions tax and the aggregate abatement standard are determined by maximizing the welfare function (3), given the best available estimates of b and c . Let the tax be $\tilde{t}$ and the abatement quota be $\tilde{q}$, which are chosen to maximize (3) with $b = \tilde{b}$ and $c = \tilde{c}$. We will calculate $\tilde{t}$ and $\tilde{q}$ in the next section.⁸ The welfare loss incurred with policy $\tilde{p} \in (\tilde{t}, \tilde{q})$, when b and c differ from $\tilde{b}$ and $\tilde{c}$ is denoted $L(\tilde{p}, b, c)$. The policy maker would like low welfare loss, and therefore specifies L_c to be the largest acceptable loss. An important result of our analysis will be to evaluate the reliability of attaining any specified level of loss.

⁷Strictly speaking the abatement cost function is the minimum abatement cost function. Implicitly, we assume that abatement responsibilities are allocated among the pollution sources to minimize the aggregate costs of achieving each level of aggregate abatement. This can be achieved with an emissions tax or with a competitive tradable emissions permit policy.

⁸It is worth noting that $\tilde{t}$ and $\tilde{q}$ are the same price and quantity policies that are derived in conventional analyses of prices vs. quantities. Under the conventional approach to this problem, the expected values of the errors in the intercepts of the marginal benefit and cost functions are assumed to be zero. Maximizing expected welfare then leads to $\tilde{t}$ and $\tilde{q}$.

The robustness-against-uncertainty of policy $\tilde{p}$ is the greatest horizon of uncertainty in the intercepts of the marginal benefit and cost functions (i.e., α) up to which all realizations of these functions result in loss no greater than L_c . Formally

$$\hat{\alpha}(\tilde{p}, L_c) = \max \left\{ \alpha : \left(\max_{b, c \in U(\alpha, \tilde{b}, \tilde{c})} L(\tilde{p}, b, c) \right) \leq L_c \right\}. \quad (5)$$

For policy $\tilde{p}$, we will demonstrate that $\hat{\alpha}(\tilde{p}, L_c) = 0$ for $L_c = 0$. This implies zero robustness to zero loss; that is, only zero error in the estimates of the b and c can produce zero welfare loss. This is true of any regulation that is based on best estimates of model parameters. Furthermore, we will show that $\hat{\alpha}(\tilde{p}, L_c)$ is strictly increasing in L_c , which implies that greater robustness to estimation error is only achievable by tolerating a greater loss; that is, robustness to error trades off against loss, and $\hat{\alpha}(\tilde{p}, L_c)$ quantifies this tradeoff.

The main result of this paper is a determination of the relative robustness of the emissions tax, $\tilde{t}$, and the abatement standard, $\tilde{q}$. Specifically, $\tilde{t}$ is more robust to estimation error than $\tilde{q}$ if $\hat{\alpha}(\tilde{t}, L_c) > \hat{\alpha}(\tilde{q}, L_c)$; if the inequality is reversed, the abatement standard is more robust. In the first case, $\hat{\alpha}(\tilde{t}, L_c) > \hat{\alpha}(\tilde{q}, L_c)$ reveals that the range of error in the estimates of the intercepts of the marginal benefit and cost functions for which an environmental authority is certain that the loss from error will not exceed a critical value, L_c , is greater under the emissions tax than under the abatement standard. Thus, the authority is more confident about limiting the loss from error under the emissions tax than under the abatement standard. Of course, if $\hat{\alpha}(\tilde{t}, L_c) < \hat{\alpha}(\tilde{q}, L_c)$, then the authority is more confident about limiting the welfare loss from estimation error under the abatement standard.

3. Info-gap analysis of price-based vs. quantity-based environmental regulation

In this section, we derive the robustness functions for an emissions tax and an aggregate abatement standard, both of which are determined with the best-available estimates of the intercepts of the marginal benefit and cost functions and the info-gap models for uncertainty in those estimates.

3.1. Robustness of an aggregate abatement standard

If the intercepts of the marginal benefit and cost functions were known, the environmental authority would choose an aggregate abatement standard to maximize the welfare function

$$W(q; b, c) = (b - c)q - (B'' + C'')q^2/2,$$

which leads to $q^* = (b - c)/(B'' + C'')$. However, with only its best estimates of b and c , the authority sets the abatement standard to maximize $W(q; \tilde{b}, \tilde{c})$, and therefore, sets the abatement standard at $\tilde{q} = (\tilde{b} - \tilde{c})/(B'' + C'')$. The

welfare loss when b and c differ from $\tilde{b}$ and $\tilde{c}$ is then $L(\tilde{q}; b, c) = W(q^*; b, c) - W(\tilde{q}; b, c)$, which is calculated to be

$$L(\tilde{q}; b, c) = [(b - \tilde{b}) - (c - \tilde{c})]^2 / 2(B'' + C'').$$

The uncertainty model (4) specifies the ranges of error in the estimates of the intercepts of the marginal benefit and cost functions at any horizon of uncertainty, α : that is, $b - \tilde{b} \in [-\alpha\tilde{b}, \alpha\tilde{b}]$ and $c - \tilde{c} \in [-\alpha\tilde{c}, \alpha\tilde{c}]$. Recall that $\tilde{b}$ and $\tilde{c}$ are positive constants. The inner maximum of the definition of robustness (5) requires maximization of $L(\tilde{q}; b, c)$ with respect to b and c . In turn, this requires either $b - \tilde{b} = \alpha\tilde{b}$ and $c - \tilde{c} = -\alpha\tilde{c}$, or $b - \tilde{b} = -\alpha\tilde{b}$ and $c - \tilde{c} = \alpha\tilde{c}$. That is, for some fractional error in the estimates of b and c , α , $L(\tilde{q}; b, c)$ is maximized with respect to b and c if b is over-estimated and c is under-estimated, or if b is under-estimated while c is over-estimated. In either case

$$L(\alpha, \tilde{q}) = \alpha^2 (\tilde{b} + \tilde{c})^2 / 2(B'' + C'') \quad (6)$$

is the maximum welfare loss of $\tilde{q}$ when the fractional error in the estimates of the intercepts of the marginal benefit and marginal cost functions is α .

Now, from (5), the robustness of the abatement standard $\tilde{q}$ is the highest α for which $L(\alpha, \tilde{q}) \leq L_c$. Since $L(\alpha, \tilde{q})$ is monotonically increasing in α , we choose α to satisfy $L(\alpha, \tilde{q}) = L_c$. Solving this equation for α provides the robustness of the abatement standard $\tilde{q}$:

$$\hat{\alpha}(\tilde{q}, L_c) = \sqrt{2L_c(B'' + C'') / (\tilde{b} + \tilde{c})}. \quad (7)$$

Since $\tilde{b}$, $\tilde{c}$, B'' , and C'' are all positive constants and L_c is non-negative, $\hat{\alpha}(\tilde{q}, L_c)$ is non-negative.

The robustness function, $\hat{\alpha}(\tilde{q}, L_c)$, quantifies the greatest fractional error in the estimates of the intercepts of the marginal benefit and marginal cost functions for which the welfare loss associated with the abatement standard $\tilde{q}$ is not greater than some critical welfare loss L_c . Note that, with respect to L_c , $\hat{\alpha}(\tilde{q}, L_c)$ has a zero intercept, is monotonically increasing, and strictly concave. The zero intercept implies that there is zero robustness to zero loss; that is, the environmental authority can have no confidence in limiting the loss from estimation error to zero. That robustness is increasing in L_c implies that greater robustness only comes with tolerating a greater loss: the authority gains confidence in meeting the performance criterion as this criterion is relaxed. Finally, the concavity of $\hat{\alpha}(\tilde{q}, L_c)$ suggests that the marginal cost (i.e., the marginal increase in critical loss) of attaining greater robustness is increasing. Put another way, confidence in limiting the welfare loss increases with higher acceptable loss, but at a decreasing rate. Robustness functions are always monotonic, expressing a fundamental trade-off between robustness and performance. They are not always concave.

3.2. Robustness of an emissions tax

We now turn to calculating the robustness of an emissions tax. We demonstrate that it has the same basic characteristics of robustness to an abatement standard.

Firms in an industry will react to an emissions tax, t , by choosing their levels of abatement so that their individual marginal abatement cost functions are equal to the tax. In aggregate, then, the intersection of the tax and the aggregate marginal abatement cost function determines aggregate abatement. From $t = c + C''q$ we have $q(t) = (t - c)/C''$. Social welfare (3), in terms of an emissions tax, is then

$$W(t; b, c) = (b - c)q(t) - (B' + C'')(q(t))^2/2.$$

The tax that maximizes this social welfare function is $t^* = (bC'' + cB'')/(B'' + C'')$. With only its best estimates of b and c , however, the regulatory authority chooses $\tilde{t} = (\tilde{b}C'' + \tilde{c}B'')/(B'' + C'')$. It is easy to demonstrate that t^* produces q^* abatement, and $\tilde{t}$ produces $\tilde{q}$ abatement. The welfare loss when b and c differ from $\tilde{b}$ and $\tilde{c}$ is $L(\tilde{t}; b, c) = W(t^*; b, c) - W(\tilde{t}; b, c)$, which is calculated to be

$$L(\tilde{t}; b, c) = \frac{[(b - \tilde{b})C'' + (c - \tilde{c})B'']^2}{2(B'' + C'')(C'')^2}.$$

As with the abatement standard, the uncertainty model (4) specifies the ranges of error in the estimates of b and c , $b - \tilde{b} \in [-\alpha\tilde{b}, \alpha\tilde{b}]$ and $c - \tilde{c} \in [-\alpha\tilde{c}, \alpha\tilde{c}]$, at any horizon of uncertainty, α . In contrast to the abatement standard, however, the inner maximum of the definition of robustness (5) requires either $b - \tilde{b} = \alpha\tilde{b}$ and $c - \tilde{c} = \alpha\tilde{c}$, or $b - \tilde{b} = -\alpha\tilde{b}$ and $c - \tilde{c} = -\alpha\tilde{c}$. That is, $L(\tilde{t}; b, c)$ is maximized if both b and c are over-estimated, or if both are under-estimated. In either case,

$$L(\alpha, \tilde{t}) = \alpha^2 [\tilde{b}C'' + \tilde{c}B'']^2 / 2(B'' + C'')(C'')^2.$$

Robustness of $\tilde{t}$ is then the solution to $\arg \max_{\alpha} L(\alpha, \tilde{t}) \leq L_c$; that is

$$\hat{\alpha}(\tilde{t}, L_c) = C'' \sqrt{2L_c(B'' + C'')}/(\tilde{b}C'' + \tilde{c}B''). \quad (8)$$

Again, $\hat{\alpha}(\tilde{t}, L_c)$ is the greatest fractional error in the estimates of the intercepts of the marginal benefit and marginal cost functions for which the welfare loss associated with the emissions tax $\tilde{t}$ is not greater than some critical welfare loss L_c . With respect to L_c , $\hat{\alpha}(\tilde{t}, L_c)$ as a zero intercept, is monotonically increasing, and strictly concave. Therefore, $\hat{\alpha}(\tilde{t}, L_c)$ has the same basic structure as $\hat{\alpha}(\tilde{q}, L_c)$. However, for some L_c , $\hat{\alpha}(\tilde{t}, L_c)$ and $\hat{\alpha}(\tilde{q}, L_c)$ will normally take on different values.

4. The relative robustness of price-based and quantity-based emissions control

We are now able to compare the robustness of the emissions tax, $\tilde{t}$, to the robustness of the aggregate abatement standard, $\tilde{q}$. Using the robustness functions (7)

and (8), calculate

$$\hat{\alpha}(\tilde{t}, L_c) - \hat{\alpha}(\tilde{q}, L_c) = \frac{(C'' - B'')\tilde{c}\sqrt{2L_c(B'' + C'')}}{(\tilde{b} + \tilde{c})(\tilde{b}C'' + \tilde{c}B'')}. \quad (9)$$

Clearly, the relative robustness of $\tilde{t}$ and $\tilde{q}$ to any critical loss, L_c , depends solely on the relative slopes of the marginal benefit and cost functions, C'' and B'' . Specifically, $\tilde{t}$ is more robust to estimation error than $\tilde{q}$ if and only if the marginal cost function is more steeply sloped than the marginal benefit function: that is, $C'' > B''$. On the other hand, if $C'' < B''$, the abatement standard is more robust than the emissions tax. Note further that the difference in the robustness of the two policies increases as L_c increases. Thus, the value of one policy over the other (in terms of immunity to loss) increases as the potential loss L_c is allowed to increase. Figs. 1 and 2 illustrate the robustness functions for $\tilde{t}$ and $\tilde{q}$ when $C'' > B''$ and $B'' > C''$, respectively.

The main result of this work is that the same relative-slopes criterion that Weitzman (1974) derived to choose between price-based and quantity-based regulation applies in our case as well. However, we have demonstrated a complementary purpose for this criterion. In the conventional case, the relative-slopes criterion provides guidance about the choice between an emissions tax and an aggregate abatement standard when the policy objective

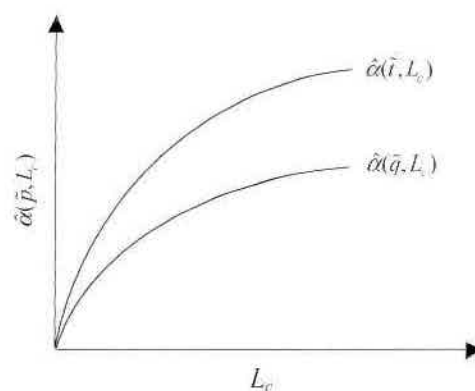


Fig. 1. Relative robustness of $\tilde{t}$ and $\tilde{q}$ when $C'' > B''$.

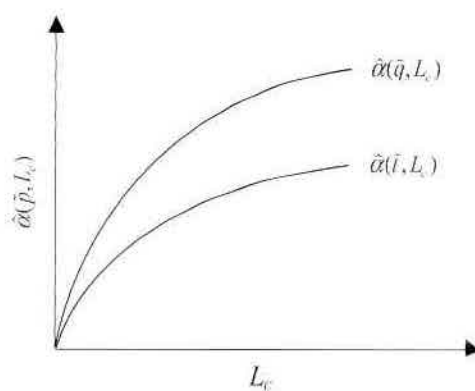


Fig. 2. Relative robustness of $\tilde{t}$ and $\tilde{q}$ when $B'' > C''$.

is to maximize expected welfare from emissions control when the errors in the estimates of the intercepts of the marginal benefit and cost functions are characterized by known moments of probability distribution functions. We have shown that the relative-slopes criterion also determines which policy is more robust to unstructured Knightian estimation error. Therefore, our work complements the conventional approach to the prices versus quantities debate, because it provides a further justification for the relative slopes criterion. Not only will this criterion lead to the policy that maximizes the expected net benefits of control under structured uncertainty, it also leads to the policy that maximizes robustness to unstructured uncertainty.

To illustrate the results of our work and the use of the info-gap approach in quantifying robustness to loss, suppose that the marginal benefit and cost parameters take on the following values: $\hat{b} = 100$, $\hat{c} = 40$, $B'' = 1$, and $C'' = 2$. In this case, $\hat{q} = 20$ and $\hat{t} = 80$. Because $C'' > B''$, $\hat{t}$ is always more robust than $\hat{q}$ (Fig. 1). To verify this for allowable loss $L_c = 100$, use (7) to calculate $\hat{\alpha}(\hat{q}, L_c = 100) = 0.175$ and use (8) to calculate $\hat{\alpha}(\hat{t}, L_c = 100) = 0.204$. That is, welfare loss from estimation error no greater than $L_c = 100$ is guaranteed with the tax policy if the estimated intercepts err by no more than $\pm 20.4\%$. In contrast, welfare loss no greater than 100 is guaranteed with the quantity policy if the estimated intercepts err by no more than $\pm 17.5\%$. That is, the robustness premium of the tax policy is $\pm 2.9\%$. For a higher allowable welfare loss, say $L_c = 300$, $\hat{\alpha}(\hat{q}, L_c = 300) = 0.303$ and $\hat{\alpha}(\hat{t}, L_c = 300) = 0.354$. At this higher level of allowed welfare loss, the robustness premium of the tax policy is $\pm 5.1\%$. In both of these cases, as well as any $L_c > 0$, the range of error in the estimates of the intercepts of the marginal benefit and marginal cost functions within which the welfare loss is limited to be no more than L_c is greater under the tax than under the abatement standard.

We can use our hypothetical numerical example to illustrate the trade-off between robustness-to-uncertainty and welfare loss, expressed by the positive slopes of the curves in Figs. 1 and 2. Whichever policy is chosen, greater robustness can only be obtained in exchange for greater welfare loss. Furthermore, this trade-off is evaluated quantitatively. For instance, a robustness of $\hat{\alpha} = 0.2$ corresponds to immunity to 20% error in the estimated intercepts, $\hat{b}$ and $\hat{c}$. For the tax policy, this corresponds to a critical welfare loss of $L_c = 96$. Pursuing greater robustness, say 40%, requires a greater critical welfare loss of $L_c = 384$.

5. Conclusion

We claim two contributions of this work. First, we have illustrated a policy evaluation tool, info-gap robust-satisficing, which is an alternative to expected welfare maximization. Info-gap robust-satisficing is useful when errors in model parameters are unstructured in the sense

that they cannot be modeled with known or confidently estimated moments of a probability distribution function. In these cases, one cannot evaluate policies in terms of their affect on expected benefits and costs. Info-gap robust satisficing requires no knowledge of underlying probability models, and evaluates policies on the basis of robustness to loss when uncertainty is unstructured. Our second contribution is that we have reinterpreted the conventional wisdom of environmental economists that the relative slopes of the marginal benefits and marginal costs of pollution control determine whether price-based or quantity-based policies should be pursued. It is conventional wisdom that the relative-slopes criterion leads to the policy type that maximizes the expected net social benefits of environmental control under structured uncertainty about social benefits and costs. We have shown that this criterion also leads to the policy choice that is more robust to unstructured uncertainty about social benefits and costs.

We applied the info-gap robust satisficing approach to the canonical model of environmental control under uncertainty that drives the conventional wisdom about prices versus quantities. It is well-known, however, that the relative-slopes criterion must be modified when there is also uncertainty in the slopes of the marginal benefit and cost functions, when the uncertainty in benefits and costs are correlated, when the marginal benefit and cost functions are nonlinear, as well as when many of the other simplifying assumptions that underlie the conventional model are relaxed (see footnotes 1 and 2). The approach we take in this paper can easily be applied to all of these more complicated situations. We believe that doing so would be a fruitful area for future research, and will lead to a deeper understanding of the design of environmental policies under uncertainty, and possibly to different policy recommendations.

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Contribution of water hyacinth (*Eichhornia crassipes* (Mart.) Solms) grown under different nutrient conditions to Fe-removal mechanisms in constructed wetlands

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Abstract

Severe contamination of water resources including groundwater with iron (Fe) due to various anthropogenic activities has been a major environmental problem in industrial areas of Sri Lanka. Hence, the use of the obnoxious weed, water hyacinth (*Eichhornia crassipes* (Mart.) Solms) in constructed wetlands (floating aquatic macrophyte-based plant treatment systems) to phytoremediate Fe-rich wastewaters seems to be an appealing option. Although several studies have documented that hyacinths are good metal-accumulating plants none of these studies have documented the ability of this plant grown under different nutrient conditions to remove heavy metals from wastewaters. This paper, therefore, reports the phytoremediation efficiencies of water hyacinth grown under different nutrient conditions for Fe-rich wastewaters in batch-type constructed wetlands. This study was conducted for 15 weeks after 1-week acclimatization by culturing young water hyacinth plants (average height of 20 ± 2 cm) in 590 L capacity fiberglass tanks under different nutrient concentrations of 1-fold [28 and 7.7 mg/L of total nitrogen (TN) and total phosphorous (TP), respectively], 2-fold, 1/2-fold, 1/4-fold and 1/8-fold with synthetic wastewaters containing 9.27 Fe mg/L. Another set-up of hyacinths containing only Fe as a heavy metal but without any nutrients (i.e., 0-fold) was also studied. A mass balance was carried out to investigate the phytoremediation efficiencies and to determine the different mechanisms governing Fe removal from the wastewaters. Fe removal was largely due to phytoremediation mainly through the process of rhizofiltration and chemical precipitation of Fe_2O_3 and $\text{Fe}(\text{OH})_3$ followed by flocculation and sedimentation. However, chemical precipitation was more significant especially during the first 3 weeks of the study. Plants grown in the 0-fold set-up showed the highest phytoremediation efficiency of 47% during optimum growth at the 6th week with a highest accumulation of 6707 Fe mg/kg dry weight. Active effluxing of Fe back to the wastewater at intermittent periods and with time was a key mechanism of avoiding Fe phytotoxicity in water hyacinth cultured in all set-ups. Our study elucidated that water hyacinth grown under nutrient-poor conditions are ideal to remove Fe from wastewaters with a hydraulic retention time of approximately 6 weeks.

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Keywords: Chemical precipitation; Fe; Phytoremediation; Rhizofiltration; Wastewaters; Water hyacinth (*Eichhornia crassipes* (Mart.) Solms)

1. Introduction

Iron (Fe) is one of the vital elements for humans and for other forms of life. Nevertheless, high doses of Fe are known to cause hemorrhagic necrosis, sloughing of mucosa areas in the stomach, tissue damage to a variety of organs

by catalyzing the conversion of H_2O_2 to free radical ions that attack cell membranes, proteins and break the DNA double strands and cause oncogene activation (Gunawardhana et al., 2002; Gurzau et al., 2003). With pathological conditions it is known that Fe metabolism and superoxide metabolism can exacerbate the toxicity of each other. Further Fe toxicity leads to diabetes mellitus, atherosclerosis and related cardiovascular diseases, hormonal abnormalities, and a dysfunctional immune system. Moreover,

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oxidative stress induced by excess Fe may also cause brain damage (Gurzau et al., 2003).

Since Fe is toxic and is a pollutant at higher concentrations developed countries such as the USA under the National Pollution Discharge Elimination System (NPDES) has enacted a permissible limit of 1.6 mg/L for inland surface waters (Ye et al., 2001a). However, developing countries such as Sri Lanka are yet to enact a permissible limit to the discharging of Fe-rich wastewaters into inland surface waters and land despite the fact that high contamination of freshwater resources and groundwaters with heavy metals such as Fe due to various anthropogenic activities such as blue-print paper, paints and pigments manufacturing facilities, laundry bluing facilities and disposal of sludges from water treatment plants has been a major environmental problem in the industrial areas over the past decades (Gunawardhana et al., 2002).

The use of advanced processes such as electrodialysis to remove low concentrations of Fe in wastewaters is not an economically feasible option in a developing country such as Sri Lanka due to the high capital, operational and maintenance costs involved. Hence, chemical precipitation following aeration seems to be still popular in Sri Lankan industries. However, chemical precipitation is also generally costly, requires intensive management and long-term maintenance, sometimes less efficient and produces a hazardous sludge, which poses disposal problems in Sri Lanka due to lack of secure landfills.

Phytoremediation is widely viewed as an ecologically acceptable alternative as opposed to the conventional physicochemical techniques of Fe removal in polluted waters. Past studies have documented the phytoremediation ability of the obnoxious free-floating freshwater weed water hyacinth (*Eichhornia crassipes* (Mart.) Solms) for nutrient-rich wastewaters (Gamage and Yapa, 2001; Jayaweera and Kasturiarachchi, 2004; Sooknah and Wilkie, 2004; Tripathi and Upadhyay, 2003). The ability of water hyacinth to remove heavy metals is also well-documented (Chua, 1998; Cooley and Martin, 1979; Cordes et al., 2000; Hardy and O'Keeffe, 1985; Kelley et al., 2000; Klumpp et al., 2002; Lytle et al., 1998; Vesk and Allaway, 1997; Vesk et al., 1999; Wang et al., 2002) though other studies have clearly manifested that hyacinths are more efficient in the phytoremediation of low concentrations of heavy metals (Hardy and Raber, 1985; Ingole and Bhole, 2003; Kay et al., 1984; Rulangaranga and Mugasha, 2003; Soltan and Rashed, 2003; Zhu et al., 1999). Nevertheless, the use of water hyacinth in constructed wetlands (floating aquatic macrophyte-based plant treatment systems) to remove Fe from wastewaters has been considered as an appealing option to make use of this nuisance weed effectively in Sri Lanka.

However, according to some authors the exact mechanisms involved in the phytoremediation of Fe and other heavy metals by metal-accumulating plants seem to be poorly understood and therefore need further study

(Brennan and Shelley, 1999; Gopal, 1987; Kumar et al., 1995). Moreover, research pertaining to the ability of water hyacinth and/or other plants to phytoremediate heavy metals at different nutrient concentrations in wastewaters is very scarce to our knowledge, though Ingole and Bhole (2003) has argued that phytoremediation of heavy metals is often increased when plants are cultured in wastewaters containing high levels of macronutrients. Therefore in this paper, we report the phytoremediation efficiencies of water hyacinth grown under different nutrient conditions for Fe-rich industrial wastewaters in batch-type constructed wetlands. This paper also attempts to describe different mechanisms involved in removing Fe from wastewaters in order to optimize the removal rates through proper manipulation.

2. Materials and methods

2.1. Experimental set-up

In this study, we attempted to simulate the phytoremediation scenarios of a Fe-rich industrial wastewater in six constructed wetlands (floating aquatic macrophyte-based plant treatment systems) comprising water hyacinth stands grown under different nutrient conditions. This was carried out as a batch study for a period of 15 weeks in an outdoor tropical environment using six fiberglass tanks each having a capacity of 590 L. Each tank was filled with 300 L of pipe-borne water and 30 healthy young water hyacinths (average height of 20 ± 2 cm) collected from selected locations at Bolgoda Lake, Sri Lanka were introduced into each tank. These plants were first acclimatized for a period of 1 week without any added nutrients. In one of the tanks (referred to as 0-fold) water hyacinth plants were cultured without any nutrient addition other than Fe as a heavy metal and different culture solutions of nutrients were introduced to the remaining tanks after the acclimatization period. A nutrient solution containing 28 and 7.7 mg/L of total nitrogen (TN) and total phosphorus (TP), respectively (i.e., 1-fold) was used as the standard nutrient solution (Table 1) based on the recipes used in other studies (Jayaweera and Kasturiarachchi, 2004; Sato and Kondo, 1981, 1983). From this standard 1-fold concentration of

Table 1
Mineral nutrient composition of the standard (1-fold) culture solution

Chemical	Concentration (mg/L)
$\text{NH}_4\text{H}_2\text{PO}_4$	28.8
KNO_3	75.8
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	184.9
$\text{CaCl}_2 \cdot 7\text{H}_2\text{O}$	73.5
NaNO_3	85.0
EDTA-Fe	18.0
H_3BO_3	1.2
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	0.7

Source: Jayaweera and Kasturiarachchi (2004), Sato and Kondo (1981, 1983).

nutrients, other concentrations of 2-fold (56 TN mg/L and 15.4 TP mg/L), 1/2-fold, 1/4-fold and 1/8-fold were made and added accordingly to different tanks. Simultaneously Fe-rich industrial wastewaters were synthetically prepared by stocking the water in each tank with A.R. grade $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to yield a contaminant concentration of 9.27 Fe mg/L. This concentration of Fe (9.27 mg/L) was selected for the study based on a previous study carried out by Gunawardhana et al. (2002). Nutrient solutions were added once in 3 weeks (except in the 0-fold) to supplement the essential nutrients that are required for plant growth and this was done after the harvesting of plants and sampling of wastewaters and sediments for Fe analysis (see below). To counter water loss due to evapotranspiration at the higher ambient temperatures, pipe-borne water was added (i.e., when required) to maintain the original level.

2.2. Sampling and analysis

From each tank two plants were randomly harvested each week. The harvested plants were not rinsed in desorbing solvents and the plants were separated into aerial tissues (stems and leaves) and roots. The separate parts were oven dried at 70–80 °C for 48 h in order to determine the dry weights. Three 1 g samples of these oven dried separate tissues were then ashed in a muffle furnace at 550 °C for 4 h. The ash was transferred to a 100 mL Pyrex conical flask containing 10–15 mL of conc. HCl (which was diluted to a 1:1 ratio) and the ash-conc. HCl mixture was heated for 10 min using a steam bath (i.e., until the ash completely dissolved and the mixture turned pale or dull yellow in color). Thereafter the resulting solution was cooled and then filtered to a 100 mL volumetric flask. The filtrate was diluted to 100 mL with distilled water prior to the analysis of Fe.

Grab samples of wastewaters were also collected in duplicate at the time of harvesting the plants and the samples were acidified to a pH less than 2 with conc. HNO_3 . The samples were then acid digested in an autoclave at 120 °C and 1.5 psig for 30 min using a sample volume of 100 mL, 5 volumes of conc. HCl and 1 volume of conc. HNO_3 (ASTM D1971-91, 1991). The acid-digested samples were re-filtered and the filtrates were topped up to 100 mL with distilled water prior to Fe analysis.

Simultaneously sediments including detritus produced by senescing plants were also collected once a week by placing three equal sized Petri dishes at the bottom of each tank. All sediments were collected by placing an inverted Petri dish on each of the three Petri dishes. The sediment samples were first filtered, and then oven dried at 70–80 °C for 24 h. Acid digestion was performed using 100 mL of distilled water as for the wastewater samples (ASTM D1971-91, 1991). The acid-digested samples were re-filtered and the filtrates were also topped up to 100 mL with distilled water prior to analysis.

All the wastewater, plant and sediment Fe extracts were acidified and stored at a temperature less than 2 °C until

analysis was performed. Quantitative analysis of Fe was carried out using a flame atomic absorption spectrophotometer (GBC 932 Plus, Australia) at a wavelength of 248.3 nm. This metal was analyzed in the atomic absorption spectrophotometer using an air/acetylene flame. In addition to analysis of Fe dissolved oxygen (DO) levels and pH of the constructed wetlands were also measured each week. DO levels were analyzed using the Winkler's Method with azide modification (APHA, 1995) and pH was measured using an electrode (EcoScan pH 6, Singapore).

Prior to the commencement of the study some root samples were also collected from each set-up using sterile containers in order to identify the presence of any Fe^{2+} -oxidizing chemolithotrophic and heterotrophic bacteria. The dilution plate method was used to determine the densities expressed as the number of colony formation units (CFU) per 1 g of roots by wet weight. Sterile nutrient agar was used for the root samples in duplicate. All the dilutions were prepared using a standard solution of 10^{-2} (i.e., 1 g of roots dissolved in 99 mL of sterile distilled water). Total number of colonies and different types of colonies (depending on colony morphology) were counted after an incubation period of 24 h at 28 ± 1 °C. Bacterial differentiation was initially done by using morphological features of colonies and an identification number was given to each morphologically different colony. All the pure cultures were prepared by streak plate method using nutrient agar medium and stock cultures were prepared using nutrient agar slants for further identification processes. Finally bacterial identification was carried out using a scanning electron microscope (Topcon Scanning Electron Microscope ABT-32, Japan), morphological features (i.e., Gram staining technique) and biochemical characteristics of cells in accordance to Bergey's Manual (Buchanan and Gibbons, 1974).

2.3. Variation of Fe in different components of the constructed wetlands

A detailed mass balance analysis was carried out using a Microsoft Excel 2003 spreadsheet incorporating continuity equations for the mass of Fe in the whole system. After the completion of the mass balance the amount of Fe partitioned into each component of the wetlands at any given time period was expressed as a percentage for that particular time period. This mass balance was also used to evaluate the different mechanisms involved in the removal of Fe from the wastewaters at different nutrient conditions.

3. Results and discussion

3.1. Key mechanisms of Fe removal from the wastewaters and optimum phytoremediation efficiencies of water hyacinth grown under different nutrient conditions

Analysis of the initial wastewater solutions (i.e., approximately 6 h after the addition of Fe) showed that

the amount of Fe were about 69%, 69%, 74%, 62%, 69% and 65% in the 2-fold, 1-fold, 1/2-fold, 1/4-fold, 1/8-fold and 0-fold set-ups, respectively (Fig. 1). Simultaneously a milky-white, cloudy appearance was noticed in the wastewater surfaces in all set-ups suggesting the formation of Fe-rich colloids (precipitates). Generally precipitation of Fe occurs following the atmospheric- (abiotic) and bacterial-mediated oxidation (mediated by *Thiobacillus ferrooxidans* and bacteria of the genera *Sphaerotilus*, *Metallogenium* and *Crenothrix*, etc.) of Fe^{2+} to Fe^{3+} (Groudeva et al., 2001; Vymazal, 1995). In this study, the added Fe (including

EDTA-Fe that was added as a nutrient except in the 0-fold set-up) was chemically precipitated as hydrous oxides (Fe_2O_3) and hydroxides/oxyhydroxides ($\text{Fe}(\text{OH})_3$ or FeOOH) following the diffusion of sufficient O_2 at the air-wastewater interfaces. This is because at the time of commencement of the study the DO levels in the 6 set-ups were high in the range of 7.25–7.45 mg/L since there was a low coverage of the tanks by the young plants (Fig. 2). Similarly, the Eh in the 6 set-ups were high in the range of 317–319 mV at the time of commencement of the study (data not shown). In other words, there seemed to be

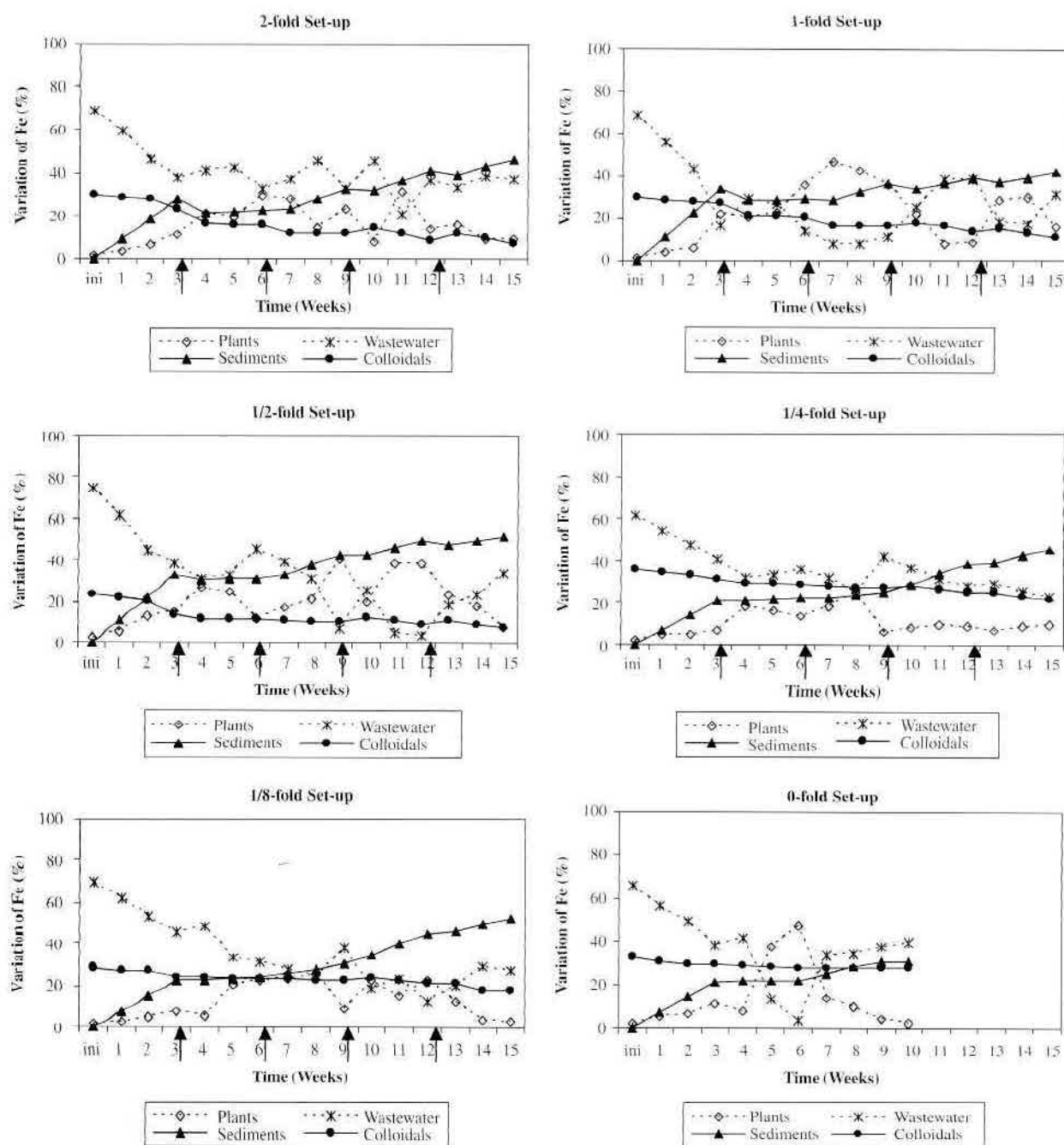


Fig. 1. Variation of total Fe as a percentage in different components of the constructed wetlands. The arrows denote the time at which the nutrients were added and "ini" refers to the initial week of nutrient addition.

insignificant bacterial-mediated oxidation and precipitation of Fe, which are slow reactions in comparison with chemical precipitation. Further the results of our bacterial identification test carried out prior to the commencement of the study revealed that bacteria of various genera are present in the roots of water hyacinth (bacteria of the genera *Azotobacter*, *Bacillus*, *Enterobacter*, *Pseudomonas* and *Staphylococcus* seemed to be more predominant) but the presence of Fe^{2+} oxidizing chemolithotrophic and heterotrophic bacteria was insignificant (Table 2). Moreover, the initial pH (i.e., the pH of the pipe-borne water added to the tanks prior to the addition of Fe) was between 6.07 and 6.25 in all the set-ups (Fig. 3). It is noteworthy that chemical precipitation of Fe occurs in the pH range of 3.5–9 (Metcalf et al., 2003; Potgieter et al., 2005; Ye et al., 2001a, 2001b) whereas any bacterial-mediated oxidation of Fe^{2+} and subsequent precipitation is only likely at low pH conditions (Vymazal, 1995). Nevertheless, these facts further justifies that any direct involvement of bacteria in the oxidation of Fe^{2+} and subsequent precipitation was an insignificant process in this study. Basically our results implied that the average pH of Fe-rich industrial wastewaters and the pH of the pipe-borne water added to the constructed wetlands (i.e., prior to introducing the wastewaters) is conducive for Fe removal to occur through chemical precipitation (provided DO levels

are higher than 3–4 mg/L for the abiotic oxidation of Fe^{2+} to occur).

According to the results of this study chemical precipitation seemed to be a dominant contribution to Fe removal especially during the first 3 weeks of the study in view of the fact that there was a fairly rapid accumulation of Fe-rich sediments in all set-ups (Fig. 1). Since a significant amount of the added Fe formed Fe-rich colloidal particles, the wastewaters appeared to be milky-white and cloudy for a period of at least 3 weeks and the highest turbidity levels were reported during the initial week (i.e., approximately 6 h after the addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) amounting to 33.40, 22.40, 18.90, 9.38, 12.60 and 13.10 NTU in the 2-fold, 1-fold, 1/2-fold, 1/4-fold, 1/8-fold and 0-fold set-ups, respectively (data not shown). Further the initial pH of all the set-ups drastically reduced to a range of 3.8–4.46 during the initial week (i.e., approximately 6 h after the addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and the average pH remained acidic in the range of 3.07–4.91 during the first 3–4 weeks of the study (Fig. 3) suggesting that acidity was generated due to the abiotic oxidation of Fe^{2+} and hydrolysis of Fe^{3+} (Amils et al., 2002; Kosolapov et al., 2004; Otero and Macías, 2002).

Although chemical precipitation occurred (with some possible coprecipitation of Mn^{2+} and phosphates) and this process was more predominant during the first 3 weeks of

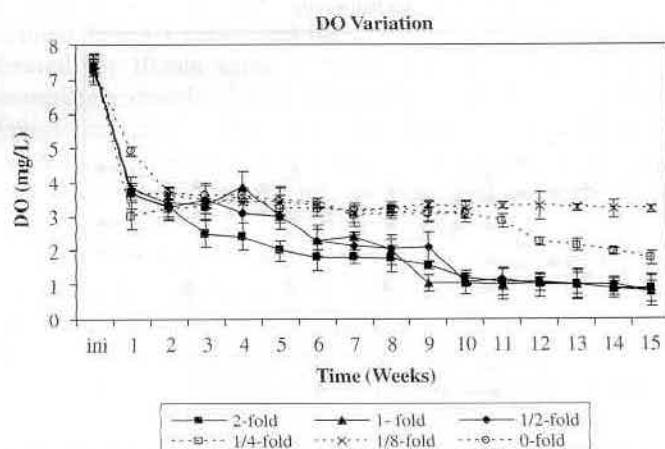


Fig. 2. Variation of DO levels. Note that DO analysis was not carried out in the 0-fold set-up after the 10th week since almost all the plants were dead and even decomposed. Vertical bars denote standard errors ($n = 3$).

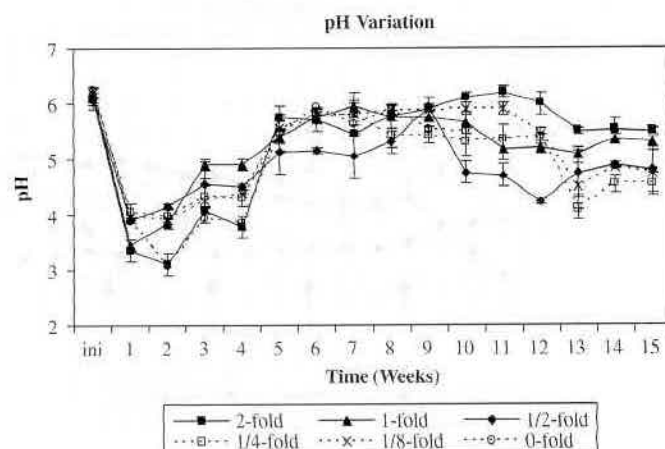


Fig. 3. Variation of pH. Note that pH readings were not taken in the 0-fold set-up after the 10th week since almost all the plants were dead and even decomposed. Vertical bars denote standard errors ($n = 3$).

Table 2

Predominant types of bacteria present in the roots of water hyacinth prior to the commencement of the study

Bacterial type	Density (CFU/g)					
	2-fold set-up	1-fold set-up	1/2-fold set-up	1/4-fold set-up	1/8-fold set-up	0-fold set-up
<i>Azotobacter</i>	5×10^4	1×10^4	1×10^4	$1.8\text{--}2 \times 10^5$	$1.6\text{--}2 \times 10^5$	$1.9\text{--}2.1 \times 10^5$
<i>Bacillus</i>	$1\text{--}2 \times 10^4$	$1\text{--}3 \times 10^4$	1×10^4	1×10^4	1×10^4	$1\text{--}2 \times 10^4$
<i>Enterobacter</i>	1×10^4	1×10^4	$1.4\text{--}2.3 \times 10^4$	1×10^4	1×10^4	$3\text{--}4 \times 10^4$
<i>Pseudomonas</i>	$1\text{--}2 \times 10^4$	$3\text{--}4 \times 10^4$	$3\text{--}6 \times 10^4$	$2\text{--}4 \times 10^4$	$2\text{--}3 \times 10^4$	$4\text{--}6 \times 10^4$
<i>Staphylococcus</i>	$1\text{--}3 \times 10^4$	$3\text{--}4 \times 10^4$	1×10^4	$1.5\text{--}1.8 \times 10^4$	$3\text{--}4 \times 10^4$	$2.8\text{--}3.4 \times 10^5$

the study it was noticed that as the study progressed most of the remaining Fe-rich colloidal particles in the wastewaters (hence the turbidity levels) showed a gradual reduction beneath the plant roots. Simultaneously the rate of Fe-rich sediment accumulation in the 6 set-ups seemed to be a gradual process. In other words, there seemed to be no complete sedimentation of these flocculated Fe-rich colloids as the study progressed and at the end of the study it was observed that the colloidal Fe content was only 7%, 11%, 7%, 22% and 18% in the 2-fold, 1-fold, 1/2-fold, 1/4-fold and 1/8-fold set-ups, respectively. Similarly, in the 0-fold set-up the colloidal Fe content remained unchanged more or less at 28% from the 5th week (Fig. 1).

Since the rate of Fe-rich sediment accumulation in the 6 set-ups occurred gradually with time (Fig. 1), this study also elucidated that apart from slow flocculation rates and subsequent sedimentation of Fe-rich colloids, senescing plants too tend to produce Fe-rich organic detritus (especially from the roots). As a consequence these organic detritus particles (being negatively charged) may have complexed with any settled precipitates of Fe_2O_3 and $\text{Fe}(\text{OH})_3$ through adsorption mechanisms. Therefore detritus may have served as adsorption (through cation exchange) sites for Fe^{2+} remaining in the wastewaters (Groudeva et al., 2001; O'Sullivan et al., 2004; Ye et al., 2001a,b). This phenomenon may have occurred to a certain extent with time especially in the nutrient-rich set-ups since plant growth and vegetative reproduction seemed to be much higher than those in the nutrient-poor set-ups and hence more detritus accumulation.

However, this study manifested that sulfate-reducing bacteria (SRB)-mediated dissimilatory SO_4^{2-} reduction with subsequent precipitation of FeS and FeS_2 did not play a significant contribution to Fe removal as the study progressed. This is because the Eh in the wastewater columns did not reduce to low values in the range of -200 to -100 mV (data not shown), though DO depletions were noticed as the study progressed especially in the nutrient-rich 2-fold, 1-fold and 1/2-fold set-ups due to rapid vegetative reproduction of the plants and hence high plant coverage of these set-ups (Fig. 2). The acidic pH conditions induced after the commencement of the study (with pH values less than 5) would have suppressed potential proliferation of SRB (Amonette et al., 2003; Fig. 3). However, in the case of the nutrient-rich set-ups it is unlikely that the occurrence of low levels of DO with time may have significantly suppressed any SRB proliferation (Fig. 2). This is because certain SRB strains have been reported to tolerate and even consume very low levels of oxygen to a certain extent, though SRB are traditionally described as obligate anaerobes (Achá et al., 2005; Okabe et al., 1999; Santegoeds et al., 1998).

In addition to chemical precipitation and subsequent sedimentation of flocculated Fe-rich colloids, phytoremediation of Fe by water hyacinth also governed Fe removal from the wastewaters, though phytoremediation seemed to be not very substantial in comparison with

chemical precipitation of Fe and was not a continuous process due to active effluxing as a means of avoiding phytotoxicity (Fig. 1). It was evident that rhizofiltration is the predominant mechanism of phytoremediation of Fe since a substantial portion of the phytoremediated Fe was highly localized in the hyacinth roots (Fig. 4). It seems that in water hyacinth phytoextraction of Fe is poor possibly due to some physiological barriers to Fe transport to aerial tissues (Garbisu and Alkorta, 2001; Zhu et al., 1999). Most likely the assimilated Fe may have formed precipitates of carbonates or phosphates immobilizing them in apoplastic and symplastic compartments in root tissues (Garbisu and Alkorta, 2001). Previous studies documented that Fe concentrations in roots were linearly negatively correlated to the solubility (as $\log K_{sp}$) of FeCO_3 (Cooley and Martin, 1977; Cooley and Martin, 1980; Cooley et al., 1979). Moreover, the adsorption of Fe to anionic sites such as phosphate and carboxyl groups in the cell walls and/or the precipitation of Fe_2O_3 and $\text{Fe}(\text{OH})_3$ within the cell walls may have accounted for high rhizofiltration (Kelley et al., 2000; Soltan and Rashed, 2003; Vesik et al., 1999).

In our study it was noticed that some of the Fe-rich colloids formed after chemical precipitation did neither remained in the wastewaters nor settled, but were adsorbed by the fine hyacinth root hairs possibly for solubilization and subsequent assimilation through the secretion of organic acids. In fact, the acidic pH conditions induced after the addition of Fe and the fact that average pH variation was within the range of 3.07–4.91 during the first 3–4 weeks of the study (Fig. 3) may also imply that apart from the abiotic oxidation of Fe^{2+} and subsequent hydrolysis of Fe^{3+} , water hyacinth exhibited a deprotonation reaction to enhance the phytoremediation of Fe^{2+} as well as to solubilize the root hair adsorbed Fe-rich colloidal particles (Soltan and Rashed, 2003). This observed adsorption of Fe-rich colloids may have been attributed to the fact that the surfaces of the fine root hairs of water hyacinth not only provide extraordinarily large surface areas with high affinity chemical receptors, but are also known to be specifically evolved with pH-dependent charged sites for the effective adsorption of Fe (Bhainsa and D'Souza, 2001; Hardy and O'Keeffe, 1985; Hardy and Raber, 1985; Matagi et al., 1998; Meagher, 2000; Soltan and Rashed, 2003).

Recent studies documented that the daily net growth rate of water hyacinth is at optimum when the plants have attained 5–6 weeks of age and moreover nutrient removal optimized during the period of optimum growth (Jayaweera and Kasturiarachchi, 2004). Since Fe is also a vital element to plants in certain concentrations it was expected that water hyacinth would optimize phytoremediation of Fe during the period of optimum growth. Nevertheless, our results elucidated that except for the water hyacinth cultured in the 0-fold set-up, water hyacinth cultured in the 2-fold, 1-fold, 1/2-fold, 1/4-fold and 1/8-fold set-ups optimized phytoremediation during the period of 11th, 7th, 9th, 8th and 8th week, respectively, with phytoremediation

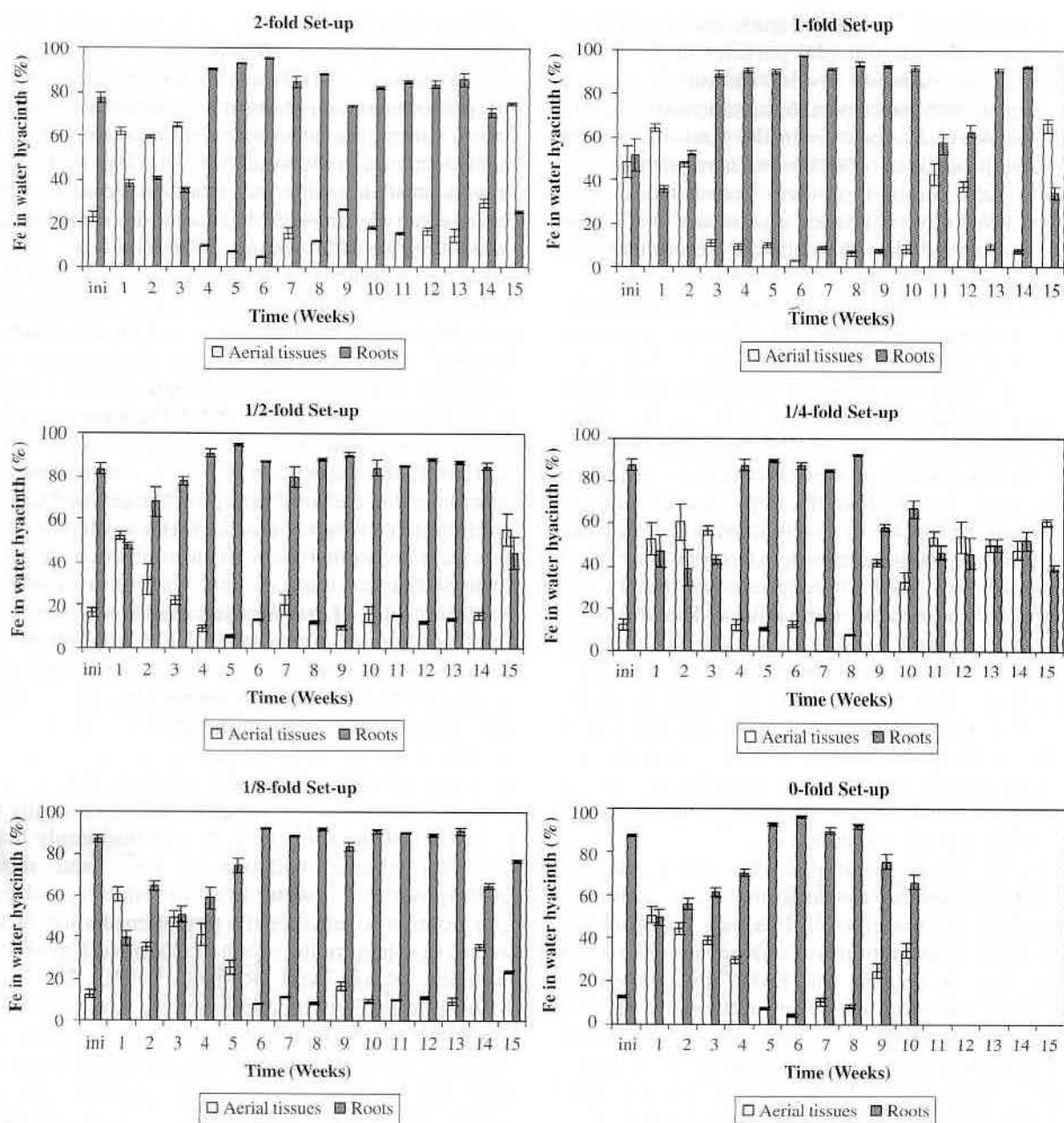


Fig. 4. Average variation of the amount of Fe in the aerial tissues and roots of water hyacinth by dry weight. Note that "ini" denotes the initial week during which the nutrients were added.

efficiencies of 31%, 46%, 41%, 25% and 25%, respectively (Fig. 1). These observations suggest that there was an optimum adsorption of Fe to root hairs when the pH of the wastewaters were between 5.92 and 6.23 (Figs. 1 and 3), which range is reported as favorable for metal ion adsorption (Baig et al., 1999; Bhainsa and D'Souza, 2001; Diniz and Volesky, 2005; Gardea-Torresdey et al., 1995; Hardy and Raber, 1985; Schneider and Rubio, 1999).

Water hyacinths cultured in the 0-fold set-up were most efficient in phytoremediating Fe as these plants showed a highest removal efficiency of 47% during the period of optimum growth at the 6th week (Jayaweera and Kasturiarachchi, 2004; Fig. 1). These plants showed a

highest accumulation of 6707 Fe mg/kg dry weight at the 6th week (Table 3) and the concentration of Fe remaining in the wastewater was around 0.28 mg/L (i.e., a highest Fe removal efficiency of about 96.98% was achieved from the wastewater with a Fe content in wastewater substantially lower than the US NPDES stipulated limit of 1.6 mg/L for inland surface waters) (Fig. 1). Similarly, water hyacinth cultured in the 1/8-fold set-up showed a fairly high accumulation of 4332 Fe mg/kg dry weight (Table 3) though these plants showed an optimum removal of only 25% at the 8th week leaving only 24% of Fe (i.e., approximately 2.51 Fe mg/L) in the wastewater (Fig. 1). In contrast, water hyacinths cultured in the nutrient-rich

Table 3
Maximum Fe accumulations in water hyacinth grown under different nutrient conditions

Set-up	Fe concentration (mg/kg dry weight)
2-fold	1905
1-fold	2483
1/2-fold	2793
1/4-fold	1918
1/8-fold	4332
0-fold	6707

2-fold, 1-fold and 1/2-fold set-ups showed a maximum accumulation of 1905 Fe mg/kg dry weight, 2483 Fe mg/kg dry weight and 2793 Fe mg/kg dry weight (Table 3) for the corresponding optimum phytoremediation efficiencies of 31% during the 11th week, 46% during the 7th week and 41% during the 9th week, respectively (Fig. 1). From the view of phytoremediation, a good accumulator should have an ability to take up more than 0.5% dry weight of a given element (Zhu et al., 1999). Hence, this study justified that water hyacinth grown under nutrient-poor conditions are very good or better Fe accumulators (in comparison with the plants grown under higher nutrient conditions) since the plants in the 0-fold set-up accumulated at least 0.67% dry weight of Fe during the period of optimum phytoremediation.

Since the plants cultured in the 0-fold set-up showed the highest Fe removal efficiency during the period of optimum growth, our results also confirmed that under completely nutrient-starved or very poor nutrient conditions phytoremediation of Fe is most efficient during the optimum growth of young hyacinth tissues. This luxury Fe uptake by the plants cultured in the 0-fold set-up was possibly attributed to the fact that the mechanisms involved in root uptake of essential elements as Fe was probably activated during nutrient-starved conditions. A similar phenomenon was observed by Kumar et al. (1995) pertaining to the root uptake of Pb^{2+} by the terrestrial plant *Brassica juncea*. Our scanning electron microscopic analysis of the water hyacinth roots collected from the 0-fold set-up showed the presence of more micro-roots along with more root elongation in comparison with the root specimens collected from the nutrient-rich set-ups. These plant-induced morphological changes in the roots may have further enhanced phytoremediation by means of providing a higher surface area for adsorption and assimilation of Fe^{2+} - and Fe-rich colloidal particles. Moreover, intense anthocyanin pigmentation was noticed in the water hyacinth roots of the 0-fold set-up probably as a response against nutritional stress. This anthocyanin pigmentation also may have enhanced Fe uptake and sequestration (Pilon-Smits and Pilon, 2002) as was observed in terrestrial plants such as the *Brassica rapa* and *Brassica juncea* in the sequestration of tungsten (W) and molybdenum (Mo) (Hale et al., 2002).

3.2. Mechanisms of water hyacinth to counteract Fe phytotoxicity

Although the plants cultured in the 0-fold set-up showed higher phytoremediation efficiencies during the 6th week, the very high levels of Fe concentrated eventually caused intense phytotoxicity such that stunted growth, chlorosis of leaves with reddish-brown spots and streaks as also observed in the study conducted by Farago and Parsons (1983) and necrosis of all tissues was evident since the 6th week. Simultaneously substantial active effluxing possibly through the roots and with time leaching of Fe from the necrosing tissues were the key mechanisms as the amount of Fe in the wastewater drastically increased to 40% (i.e., approximately 3.71 Fe mg/L) at the 10th week. In fact, after the 10th week almost all the plants in the 0-fold set-up were found to be dead and even decomposed. Therefore a further chemical analysis of Fe in the wastewaters, sediments and plant tissues was discontinued (Fig. 1).

Plants cultured in other set-ups also showed significant active effluxing intermittently and with time possibly to prevent any phytotoxic levels of Fe being accumulated (Fig. 1). According to our mass balance analysis root-mediated precipitation (possibly Fe as $FePO_4$ or $FeCO_3$) and subsequent sedimentation of Fe flocs was also noticed to a very minor extent during most periods of active effluxing to avoid Fe phytotoxicity (Fig. 1). Most likely, these Fe-rich colloids were formed inside the root cells and involved a release of root exudates, probably some peptides to flocculate these colloidal particles. This mechanism of root-mediated precipitation was also identified in the mechanistic system dynamics modeling approach used by Brennan and Shelley (1999) to simulate the uptake and translocation of Pb^{2+} in maize (*Zea mays* L. cv. Helix).

Previous studies showed that hyacinth roots form plaques of $Fe(OH)_3$ by diffusing photosynthetically produced O_2 to the rhizosphere to avoid the formation of H_2S and to counteract Fe^{2+} and Mn^{2+} toxicity at lower DO levels and Eh conditions (Soltan and Rashed, 2003; Vesk and Allaway, 1997; Vesk et al., 1999). However, we hardly observed any presence of deep orange or reddish-brown root plaques of Fe in water hyacinth root surfaces as the study progressed (especially when plant cover was higher in the nutrient-rich set-ups). It seems that rhizospheric oxidation in water hyacinth is less effective than that of other free-floating plants such as pennywort (*Hydrocotyle umbellata*) and submersed macrophytes (Carpenter and Lodge, 1986; Sooknah and Wilkie, 2004).

3.3. Photoreduction of Fe and recycling of Fe^{2+} in the constructed wetlands

The present study in agreement with other studies (Groudeva et al., 2001; O'Sullivan et al., 2004; Ye et al., 2001a, b) revealed that constructed wetlands are effective in the removal of Fe from wastewaters. However, some

studies have manifested that during the daytime Fe^{3+} could undergo photoreduction into water soluble Fe^{2+} , hence resulting in mobilization or recycling of Fe (Collienne, 1983; Goulet and Pick, 2004; McKnight et al., 2001). Further it is reported that photoreduction mechanisms are enhanced at low pH conditions and in the presence of organic matter (Collienne, 1983; McKnight et al., 2001). However, in this study photoreduction of Fe^{3+} to Fe^{2+} seemed to be insignificant considering the fact that there were no time periods manifesting any drastic dissolution of Fe-rich colloids and the settled Fe-rich sediments with a concomitant recycling of Fe back to the wastewaters (Fig. 1). One possibility is that the water hyacinth plants having a rapid growth and vegetative reproduction rate resulted in a rapid proliferation, thereby effectively shielding the bottom of the tanks against ultraviolet radiation. This seemed to be more predominant in the case of nutrient-rich set-ups. It is reported that photoreduction scenarios are anticipated to be significant in wetlands only when the plant cover is low or absent in the littoral areas (Goulet and Pick, 2004). Also as explained earlier some of the Fe-rich colloids present in the wastewater columns were effectively trapped by the water hyacinth root hairs for subsequent solubilization and assimilation of Fe through the secretion of organic acids, hence further reducing the exposure of the Fe-rich colloids to ultraviolet radiation.

4. Conclusions

The results obtained revealed that chemical precipitation and phytoremediation largely through the process of rhizofiltration are the key mechanisms to govern the removal of Fe-rich wastewaters in batch-type constructed wetlands comprising water hyacinth stands. However, chemical precipitation seemed to be more predominant than phytoremediation especially during shorter time periods of around 3 weeks. Moreover, there may have been some coprecipitation reactions but there were insignificant oxidation and subsequent precipitation of Fe mediated by bacterial biofilms occurring in the roots of water hyacinth. Similarly, there was no evidence to manifest that SRB-mediated dissimilatory SO_4^{2-} reduction played a significant contribution to Fe removal. Also photoreduction of Fe with subsequent recycling of Fe back to the wastewaters seemed to be insignificant.

This study also elucidated that water hyacinth grown under completely nutrient-poor conditions is a promising candidate for a batch removal of Fe-rich wastewaters. Basically our results implied that young plants (i.e., plants having tiny fibrous roots with an average height of 20 ± 2 cm) reproduced by adult hyacinths inhabiting unpolluted water bodies are recommended to be operated in a pilot scale batch-type constructed wetland with a hydraulic retention time (HRT) of approximately 6 weeks. After a period of approximately 6 weeks, a complete harvesting is recommended to optimize the phytoremedia-

tion potential and also to prevent any active effluxing of Fe at phytotoxic levels.

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Problems in naming and defining the swampy meadow—An Australian perspective

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Abstract

This paper explores the confusing terminology used in the description of a landform characterised by swampy, alluvial valley floors, generally known in Australia as 'swampy meadows'. Swampy meadows were once common in the Australian landscape. Following the impacts of European settlement, such as clearing, grazing, swamp burning and draining, functionally intact systems have become rare in the contemporary landscape. Detrimental affects on swampy meadows are now increasingly being recognised, leading to a need for their restoration and conservation. Confusion over terminology and definitions, however, has hindered our capacity to understand the complex nature of these systems, and to develop appropriate management strategies and policies to protect and restore them. In particular, a multi-disciplinary understanding of their geomorphic processes, hydrology, and ecological form and function is not catered for in any single definition or characterisation that is useful to policy makers and land managers. The paper discusses the repercussions that unclear swampy meadow nomenclature has on ecological understanding, conservation policy, restoration, and land values. It concludes with the construction of a more precise taxonomic definition of the swampy meadow.

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1. Introduction

1.1. Landform of many names

At the time of early European settlement in Australia, a valley landform feature, recognised for the relative absence of trees, vegetative cover of grasses, rushes and sedges, and at times disconnected pools, was commonly ascribed as chain of ponds/chain of holes and meadows, e.g., Assistant Surveyor Evans (1814), Major Thomas Mitchell (1846), or swamps, e.g. the explorer Gregory Blaxland (1813). This landform is now relatively rare as an intact functioning system. Further, its terms may be confused with a plethora

of English language vernaculars such as dell, wet meadow, cut and fill landscape and discontinuous stream.

1.2. Terminological confusion

Most of the terms have vagaries in their description and are dependent on the user's interest, background or principle scientific discipline, country of origin, and the inherent morphology and characteristics of the system in review. An examination of the literature suggests that the 'swampy meadow type' landform has been mostly described or characterised though not necessarily defined. The confusion over terminology and definitions limits knowledge transfer, our capacity to understand their complex nature and our ability to protect and restore them. Definitional clarity is a prerequisite for any considered conservation initiative that is bound by legislature or policy. It is even more important for the setting of conservation goals. Nor do the problems with

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terminology end here. These drainage systems are affected by both natural and anthropogenic factors resulting in morphological and evolutionary changes that add to the perplexed state of confusion.

1.3. A landform under threat

The swampy meadow system is under threat from our current land use practices. The need to either protect or restore this landform system is increasingly being recognised by many stakeholders. Although natural aggrading and degrading processes have occurred in swampy meadows over geological time (Prosser, 1991; Fryirs and Brierley, 1998c), anthropogenic factors such as clearing, grazing, burning and draining since European settlement have significantly contributed to their widespread and rapid degradation (Eyles, 1977b; Prosser, 1991; Prosser and Winchester, 1996; Page and Carden, 1998). The altered state of these intact, complex systems to incised or degraded gullies (Eyles, 1977b; Wasson et al., 1998; Brierley et al., 1999; Zierholz et al., 2001; Hazell et al., 2004) is more or less synonymous with stream degradation in other parts of the world (Bull, 1997; Zierholz et al., 2001; Schilling et al., 2004).

This paper explores Australian and international English language terms used to label the swampy meadow landform; discusses terminological characteristics and constructs a more concise definition. We conclude that this definitional uncertainty in Australia is reflective of problems on a global scale.

2. Terms and their characteristics

2.1. Swampy meadow

'Swampy meadow' is an accepted term in the Australian literature, and has been adopted by several authors (Prosser, 1991; Prosser et al., 1994; Butterworth et al., 2000; Rutherford et al., 2000; Zierholz et al., 2001; McKenzie et al., 2004). This landform, with an example shown in Fig. 1, has been described by Prosser (1991) as being a swampy, alluvial valley floor without a continuous channel, vegetated to its full width with sedge and tussock grass. This term is a relatively recent addition in the literature, as Prosser recognised that the more widely adopted term, 'chain of ponds', was not always befitting the landform being studied as he reasoned not all valleys, or swampy meadows, contain chain of ponds (irregularly spaced pools).

2.2. Chain of ponds

'Chain of ponds' is the most commonly used swampy meadow synonym in the Australian oral and written, scientific and layman's language. In some instances, chain of ponds systems are contained within swampy meadows (Prosser, 1991; Fryirs and Brierley, 1998a,b; Brierley and



Fig. 1. A typical swampy meadow, located in the Neville State Forest, Neville, NSW, shows an unchannelised valley floor vegetated with sedge, rushes and tussock grass.

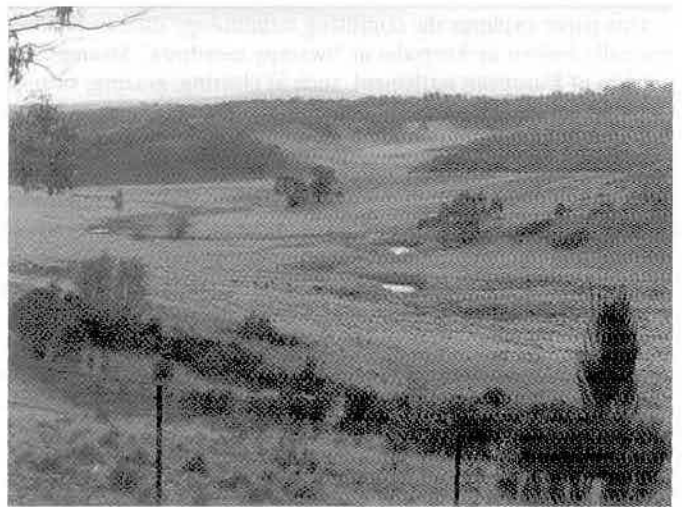


Fig. 2. A swampy meadow located in a valley in the Upper Shoalhaven of NSW, now known as Cookanulla Creek, contains disconnected pools, or a chain of ponds.

Fryirs, 2000; Zierholz et al., 2001), in which case they are characterised by a series of irregularly spaced, disconnected ponds separated by vegetated sediment bars (Eyles, 1977a) (Fig. 2). Further, Hazell et al. (2003, 2004) describes the ponds as deep, steep-sided and relatively permanent lying within flat alluvial environments, or swampy meadows. As an example of the confusion surrounding this terminology, Wasson et al. (1998) has given an example of swampy meadows contained *within* extant chain of ponds.

However, the term has not always been used synonymously for the swampy meadow landform. In the early part of European settlement in eastern Australia, numerous accounts of 'chains of ponds' and chain of holes' were noted from the historical documents of explorers and surveyors (e.g. Evans, 1814; Oxley, 1818; Richards, 1828; Darwin, 1836); a number of these refer not to swampy

meadows but to water holes in rivers during periods of low flow or drought (Eyles, 1977b; Mactaggart et al., 2007 in review).

In an equally broad context, chain of ponds is used in reference to the geomorphic waterhole development in the anastomosing channel system of Cooper Creek, in arid east-central Australia. According to Knighton and Nanson (2000), it is likened to the chains of ponds morphology detailed by Eyles (1977a), stating that they resemble discontinuous scours forming ponds. Further, Knighton and Nanson postulate that they could have formed as a result of localised scour, a similar claim to that of Eyles. In the case of Cooper Creek, these ponds are large-scale waterholes, ranging in length from 100 m to over 20 km. In contrast, lengths of ponds in south-eastern Australia are most commonly less than 50 m, and are governed by different hydrological regimes and ecological characteristics. To further heighten the confusion, the term chain of ponds has been used to label post-glacial lakes in North America, for example the locality Chain of Ponds in Maine.

2.3. Cut and fill landscape and discontinuous ephemeral stream

Coupled by their common characteristic of having discontinuous channels, the swampy meadow and chain of ponds have a common evolutionary feature. They can exhibit natural or human-induced geomorphic processes of long phases of sediment accumulation (fill) with short intervals of incision and sediment release (cut). Material deposited as valley fills are remnants from a combination of 'cut and fill' processes (Cooke and Reeves, 1976; Patton and Schumm, 1981; Prosser and Slade, 1994; Fryirs and Brierley, 1998c). Landforms shaped by these processes are referred to as cut and fill landscapes or cut and fill floodplains, and are recognised as a process-orientated or genetic classification for swampy meadows and their allied dells, swamps, dambos and chain of ponds (Nanson and Croke, 1992; Fryirs and Brierley, 1998c). In the literature, these processes are not always colloquially referred to as cut and fill. Rather as the process implies it refers to phases of aggradation (deposition) and degradation (denudation) (e.g. Bull, 1997).

Not all valley fills with phases of aggradation and degradation provide suitable environments for the development of swampy meadows. This stands to reason as they occur over a wide range of intrinsically and extrinsically diverse environments. In a very different environment, Bull (1997) describes the valley fills of western North America (discontinuous ephemeral streams) where valleys are similarly governed by processes of aggradation and degradation. During the period of early European settlement, the streams were characteristically discontinuous and ephemeral, and the landscape was described as being fertile with broad valley floors. The streams suffered a similar fate to those in Australia, and are now more readily recognised

as incised gullies (or arroyos as they are commonly known). In comparison to some Australian settings, for example the Bega catchment (refer Brierley et al., 2002), the precipitation, temperature and altitude vary widely throughout the region, and in concert with the variable lithologies, vegetation colonising these streams are also likely to be variable. Vegetation types were not described by Bull (1997), however, it can be deduced that not all would have the hydrological or ecological characteristics likened to swampy meadows, especially those in low rainfall areas where valley floors are underlain by sandy gravels.

Moreover, the development of swampy meadows are not wholly confined to cut and fill landscapes as Mäkel (1974) acknowledges. Dambos in areas of higher relative relief have developed after a 'cut and fill' phase; others on broad, flat plateaux have developed through denudational processes, and a further type has developed in conjunction with fan accumulation.

There is a degree of uncertainty in determining the terminological precision between cut and fill landscapes and the swampy meadow/chain of ponds as they are at times used interchangeably, despite the well-established understanding of their geomorphic processes. This has become problematic when the characterisation is primarily morphogenetic. A more multi-disciplinary description is necessary, and this construct is further explored in Sections 3 and 5 of the paper. Therefore, caution needs to be applied when adopting the terms 'cut and fill' and 'valley fill' to label swampy meadows, as hydrological and ecological relationships are not generally considered. Thus, the demarcation between what constitutes a valley fill and a swampy meadow is a matter of conjecture, particularly when each landform can be a continuum of the other. This relationship can occur both between and within valley fills.

2.4. Swamp

Definitions for swamps are many and varied and include, for example, three definitions noted from different sources in the US Environmental Protection Agency's Terminology Reference System (US Environmental Protection Agency (EPA/TRS), 2006) (viz):

- A permanently waterlogged area in which there is often associated tree growth, e.g. mangroves in hot climates (source: European Environment Agency, European Topic Centre on Catalogue of Data Sources: General Multilingual Environmental (Thesaurus)).
- A type of wetland dominated by woody vegetation but without appreciable peat deposits. Swamps may be fresh or salt water and tidal or non-tidal (source: Office of Communications, Education, and Media Relations: Terms of Environment: Glossary, Abbreviations, and Acronyms (Revised December 1997)).
- A type of wetland that is dominated by woody vegetation and that does not accumulate appreciable

peat deposits. Swamps may be freshwater or saltwater and tidal or nontidal (*source: EPA/Great Lakes National Program Office: Glossary of Great Lakes Ecosystem Management Terms*).

In the Australian Soil and Land Survey Field Book, McDonald et al. (1998) have defined swamps as being:

- Almost level closed, or almost closed depression with a seasonal or permanent water table at or above the surface, commonly aggraded by overbank stream flow and sometimes biological (peat) accumulation.

To add to the confusion, and to highlight the inconsistencies of terminology Moss (1988), from an English perspective, has considered swamps to be:

- Permanently wet with peaty soils, often dominated by single stands of a single tall herb species, usually a sedge or grass, or by trees.

There are two main inconsistencies in these definitions potentially leading to confusion or uncertainty. First, woody plants are characteristic of swamps in the Euro-American examples, though they are not key features in the Australian or English definitions. Secondly, the issue of peat formation is contradictory, with the EPA/TRS stating that swamps have no appreciable peat deposits, and McDonald and Moss suggesting it can be evident (though the degree of accumulation is unquantified).

It appears that the degree of similarity of swampy meadows to swamps is only as good as the definition used. The generally treeless and at times peat-forming swampy meadows are clearly dissimilar to the Euro-American swamp types, though they can be analogous to some Australian and English examples. The derivative 'meadow', then, becomes the key word in characterising the vegetative characteristic of a particular swamp type. Finally, the swamp definitions express little or no physiographic information, with the principle determinants being hydrology and vegetation structure. This allows the term to be used broadly, including swamps occurring on plateau creeks and their tributaries (Henry, 1987), in the valley floor (Buchanan, 1980; Fryirs and Brierley, 1998c) or on valley sides (Buchanan, 1980).

2.5. Dambo

It appears that the terminology and definitions of these landform systems have similarly troubled African scientists and lay persons. 'Dambo' was a word originally adopted by the local Zambians to describe various kinds of seasonally wet grass-covered and treeless areas such as floodplains or valley floors (Mäkel, 1974). Redefinition of the term in the scientific literature aimed to narrow the meaning of the term. However, the ultimate result was less than confining with the subsequent redefinition being inclusive of dambos from different geomorphic sites, such as seasonally flooded valley floors and lateral extensions of floodplains (Mäkel, 1974). As well there was a hydro-pedological definition indicating dambos are areas of

seasonally wet or permanently wet soil, or with a water-table high enough to inhibit the growth of woodland savannah trees. Confusion continued to rein for decades, compounded by countries such as Rhodesia [Zimbabwe] and South Africa employing their own terminology and sense of what they represent. Further attempts at defining dambos finally excluded the types relating to the river floodplains, with an adjusted definition given by Mäkel (1974) as: shallow, linear depressions in the headward zone of rivers without a marked stream channel (discontinuous channel), being seasonally waterlogged and grass-covered, bearing no true woodland vegetation. This definition by Mäkel combines geomorphological, hydrological, biogeographical characteristics and climatic aspects. Prosser et al. (1994) identify similarities between the Australian swampy meadows and the African dambos and in somewhat of a cultural displacement, the term 'dambo' has been used synonymously for peat-filled depressions in Chinese sub-alpine headwater zones (Qiu, 1993).

2.6. Ciénega

Spanish explorers in the American Southwest originally used the term *ciénega* in reference to riparian marshlands, and Hendrickson and Minckley (1985) note it has attained acceptance in cartographic and public vocabularies of the region. Prosser (1991) has also recognised that they are similar in form and sediments to the swampy meadow. The term is applied to a diversity of aquatic habitats throughout the areas of Hispanic influence, including floodplain lakes and a broad spectrum of marshy and swampy habitats at any elevation. As well, there are high elevation marshy to bog-like alpine and cold temperate meadowlands dominated by semi-aquatic and terrestrial grasses, sedges and rushes, and low elevation subtropical marshes in oxbows, behind natural levees and along margins of major streams, dominated by large reeds (Hendrickson and Minckley, 1985). *Ciénegas* of another form, those fed by perennial springs in headwater streams at mid-elevations of 1000–2000 m, have been defined by Hendrickson and Minckley (1985) and transcribed briefly as a system with shallow, multiple channels, vertical-walled channels and pools, controlled by permanently saturated hydrosols, with many metres of organic sediments, dominated by sedges, rushes and grasses. Further, Hendrickson and Minckley (1985) indicate that the latter form has long phases of relative stability and infrequent cycles of incision.

2.7. Dell

Dells are described by Young (1986) as small headwater valleys characteristically sediment-choked and swampy, largely treeless and dominated by sedges and shrubs. Tuckfield (1986), on the other hand, describes dells occurring in the New Forest, United Kingdom as amphitheatre-shaped hollows, perched on valley sides. These latter landforms are also known as valley side

swamps or hanging swamps, e.g. on the Hawkesbury Sandstone geologies of NSW (Buchanan, 1980).

2.8. Wet meadow

Clarity of a definition is not improved with wet meadows, this being credited to its widespread usage in different countries. In Germany it is used as a direct translation of 'Feuchtwiese', an ancient term describing watery, unproductive meadow landforms (e.g. Bauer, 1982). Further, its descriptive disparity is highlighted in the case of it being used to refer to a large freshwater, dunal wetland on the south coast of New South Wales (NSW), Australia (De Jong, 2000), also being used to describe a montane meadow vegetated with rushes (*Juncus* spp., *Eleocharis* spp.) and sedges (*Carex* spp.) in California's Sierra Nevada range (Micheli and Kirchner, 2002).

Wet meadows, by reference and inference, can include a Swiss lake marsh internationally recognised as a significant wetland (Cattin et al., 2003); a species-rich meadow in the Czech Republic (Wotavová et al., 2004); a feature on landslide deposits in northern California, being strikingly different to the surrounding xeric landscape (Lee et al., 2004); a semi-marsh wetland in Greece densely covered with low vegetation (Pyrovetsi and Crivelli, 1988) and a waterlogged meadow in Denmark covered with grasses and forbs (Schmidt et al., 2005). One particular type of wet meadow, termed the beaver meadow, is attributed to dam-building and related activities of the North American beaver (*Castor canadensis*). As a result, expansive areas of ponds and meadows (or herbaceous wetlands) are created (Johnston, 1994; Butler, 1995), with multiple surface flow paths and diversion channels (Butler, 1995).

2.9. Maya

The term 'Maya', labelling a special drainage feature in the Dinder National Park of Sudan, has been used synonymously for wet meadow by Abdel Hameed et al. (1997). These backswamp features straddle low-lying basins, river meanders and oxbow lakes and are generally crescent-like in shape. They are generally flat with slight and/or no clear banks, and include young productive wet mayas and old non-productive dry ones.

2.10. Mire, marsh and morass

Many of the terms described in Sections 2.1–2.10 are characterised by their morphological properties. The understanding of swampy meadows can be improved across scientific disciplines and globally when bridges are linked to mires and marshes, which, unlike the swampy meadow, are well understood in the scientific community in relation to their hydrologic and chemical functioning and associated ecology. The problem so far has been that they often occur, or are recognised, as different landform features to the swampy meadow, and hence are not often

used synonymously. Opportunities are then lost for comparative examination of system processes. Therefore, it is necessary to characterise these systems for comparative purposes.

The term mire has been used in a generic sense by Gore (1983), as he recognises different terms can have variable meanings. This leads to confusion as it has done in the case of the swampy meadow and its derivatives. Mires include ecosystems described in English usage such as fens, bogs, swamps, moor, muskeg and peatland (Gore, 1983) and are permanently wet and peat forming. Marshes, on the other hand, are intermittently flooded and non-peat forming (Gore, 1983; Van Breemen, 1995). Bogs are nutrient-poor and acidic (Wassen et al., 1990; Clarke and Martin, 1999; Wahren et al., 1999; Whinam et al., 2003) being attributable to a system fed by nutrient-poor rainwater (ombrotropic) (Gore, 1983; Van Breemen, 1995; Clarke and Martin, 1999) or nutrient-poor groundwater (soligenous) (Clarke and Martin, 1999). *Sphagnum*-dominated communities, forming *Sphagnum* peatlands (Clarke and Martin, 1999; Whinam et al., 2003), or *Sphagnum* bogs (Van Breemen, 1995) are associated with these environments. Fens are characteristically less acid, and richer in nutrients than bogs (minerotropic) (Wassen et al., 1990; Van Breemen, 1995; Clarke and Martin, 1999). The higher nutrient status results from solute-enriched groundwater (Van Breemen, 1995). Given particular environmental conditions, it is conceivable that a whole, or parts, of a swampy meadow system may be characteristically akin to a fen, bog or marsh.

The word morass, pertaining to a bog, fen or marshy ground in an English language dictionary, appears to be an uncommonly used word. Early references were given by explorers Captain Watkin Tench (1793) and John Oxley (1818) in NSW. The term is not recognised in the Oxford Dictionary of Ecology (Allaby, 1998), the New Penguin Dictionary of Geology (Kearey, 1996), the New Penguin Dictionary of Science (Clugston, 2004), nor the US Environmental Protection Agency, Terminology Reference System. Furthermore, there is a general omission of this word in the scientific literature.

2.11. Swampy meadows as a wetland analogue

Affiliating swampy meadows as a wetland analogue is a little like opening Pandora's Box. It is compounding one complex system with many attached synonyms, descriptions and loose definitions into another category with equally complex systems, descriptions and definitions. However, determining linkages between these two diverse landform features has significant ramifications for conservation, protection, management, land development and exploitation, and restoration. (Restoration being the process of returning an area to its original state prior to degradation, compared with rehabilitation, which is applied to areas which formerly had no growth at all; Harris et al., 1996.) These aspects are further explored in

Section 4.2.2. First, recognising what constitutes a wetland is necessary in determining the 'goodness of fit' for swampy meadows and their related terms.

A definition adopted by the Ramsar Convention, and used in the Australian wetlands directory (Environment Australia, 2001) and the commonwealth wetlands policy (Environment Australia, 1997), is wetlands are areas of marsh, fen, peatland or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt, including areas of marine water the depth of which at low tide does not exceed 6 m. An abridged version of the Ramsar definition is used in the wetlands management policy for NSW (DLWC, 1996), and defines land that is inundated with water, on a temporary or permanent basis, usually slow moving or stationary, that is shallow, or may be fresh, or that is brackish or saline. Briggs (1981) quantifies this level of inundation to be up to 2 m.

In the USA, jurisdictional wetlands are delineated by the presence of three factors: hydric soils, hydrophytic vegetation, and wetlands hydrology (frequency of flooding) (Cowardin et al., 1979; Vepraskas and Sprecher, 1997). Hydric soils, as defined by the Soil Conservation Service in 1994, are those that are formed under conditions of saturation, flooding or ponding that lasted long enough during the growing season to develop anaerobic conditions in the upper part (Vepraskas and Sprecher, 1997).

In view of seeking an association between swampy meadows and wetlands, it is not necessary to be pedantic with a wetland definition, especially as there are no universally accepted ones; rather, the intent is to scope the definitions with which swampy meadows could be aligned. Even a cursory review of the literature indicates that swampy meadows, in their broadest context, fit the analogy of a wetland. The clarity of this determination, however, is mostly by inference, and is clouded by the plethora of terms and characteristics. As well, the demarcation between what constitutes a swampy meadow and another landform feature, particularly a valley fill, is arguable, as nature is a master of the continuum. It is also very much dependent on the users' perspective. Given this, not all swampy meadows should be categorised as wetlands.

3. Coming to terms with terms

Drawing conclusive distinctions and comparisons between the terms and closely related landform features are problematic. Fundamentally, the most significant problems seem to be their general lack of definitional conciseness or definitional differences, the variable descriptions accounted in the literature and the inferences that need to be made to deduce characteristic features. This is in part due to user perspectives, differences between ecosystems, purpose of definition, problems in developing definitions, and to a lack of knowledge and understanding across scientific disciplines, different environments and regions. Some terms

have been adopted from primarily a geomorphic understanding, while others stem from other disciplines framed in consideration of ecological or hydrological attributes. These subjective factors often make for weak and imperfect comparisons. In Table 1 an attempt has been made to differentiate or classify terms into single distinguishable units based on a dichotomous key.

In Table 1, we see that some terms and their associated landforms are easily separated, and hence are dissimilar to the swampy meadow. In other cases we see an agglomeration of poorly separated terms, the general 'bunching' being symptomatic of a number of factors. First, it is suggestive of similarities, and therefore terms can be considered relatively synonymous, or having close relationships according to the classification criteria given; and secondly, the broad contextual use of the terms (e.g. chain of ponds, swamps, wetlands) suggest they have many different attributes in common with other terms; and lastly, with poor definitional clarity and similarity of characterisation, it is difficult to separate some terms into discrete units. The question now arises: does this matter?

4. Repercussions of taxonomic and definition uncertainty

Uncertain taxonomies and definitions are not only a scientific and research problem, they have significant ramifications for ecological understanding, conservation policy and planning, restoration and land values—the problem of naming nature continues.

4.1. Ecological understanding

Criteria used to distinguish landform features can become the basis of a definition. As this is based on our current knowledge and understanding it can create its own shortcomings and suite of problems. To illustrate, definitions can be misdirected and misused if there is an disparity of knowledge between disciplines, such was the experience of Joosten and De Klerk (2002) in the field of Quaternary palaeopalynology. They recognised that as this field has developed over the decades, one of its key components, the classification and nomenclature of pollen, has not developed to at the same pace. With this, pollen and spore identification have often been incorrectly or incompletely applied, resulting in confusion, misunderstanding and loss of information. As our understanding of the complexity of swampy meadows develops and our knowledge becomes more precisely integrated over time, the characterisation and definition of a swampy meadow may similarly evolve and change. It would also be expected that with additional studies there would also be a tendency towards even more confusion unless clarification is sought now.

4.2. Conservation policy

Assigning a name or a definition to a natural system can influence conservation, restoration, management,

Table 1
Dichotomous key for the differentiation of terms

1a. Continuous channel	
2a. Stream with ephemeral, semi-permanent or permanent water flow	
3a. Incision bedrock controlled, transport streams, steep slope, steps and/or pools/riffles	Upland/headwater stream
3b. Incision through colluvial or alluvial material, low gradient	Meandering, braided or anastomosing channel
4a. Continuous flow of water along channel, pools/riffles	Stream in high flow regime
4b. Period of little or no flow, discontinuous pools of water in channel induced by low flows or scours, and separated by sediment bars and/or biological accumulation	Stream during low flow regime, chain of ponds
2b. Water flows mostly intermittent	
6a. Hydrologic conditions not suitable for the development of swamp vegetation (low periodicity of flow or runoff availability, high water depth, high water velocity or stream power, bedrock substrate).	
7a. Open depression with short, precipitous walls, eroded by channelled stream flow and consequent collapse and water-aided mass movement	Gully
7b. Landform evolved through geomorphic processes of aggradation and degradation	Incised cut and fill landscape
6b. Hydrologic conditions suitable for the development of swamp vegetation (high water holding capacity of soils, perched water table, impervious subsoil, high periodicity of flow or runoff, low stream power)	Incised cut and fill, inset swampy meadow stabilised or in phase of degradation or aggradation, gully
1b. Discontinuous or no channel	
8a. Water collecting landform not part of open, linear drainage line	
9a. Not typically swampy	Closed depression, gilgai, swale, lake, dam, wetland, wet meadow, chain of ponds
9b. Has swamp characteristics (periodically or permanently saturated soils, hydrophytic vegetation, organic matter accumulation, maybe periodically inundated with shallow water, pools present or absent)	
10a. Swamps in hollows perched on valley sides	Dell, valley side swamp, hanging swamp
10b. Swamps not in hollows perched on valley sides	
11a. Permanently wet, peat forming	
12a. Landform dominated with swampy plants including trees and shrubs	Mire, fen, bog, peatland, wetland, swamp, dell, maya
12b. Landform dominated by herbaceous plants including graminoids and forbs.	Mire, fen, bog, peatland, wetland, swamp, maya, wet meadow, ciénegas
11b. Intermittently flooded and non-peat forming	Marsh, wetland, swamp, wet meadow, dell, maya
8b. Landform part of linear drainage line in valley floor which may have multiple flow pathways	
13a. Hydrologic or geomorphic conditions not suitable for the development of swampy vegetation (low periodicity of flow or runoff availability, high stream power, porous soils, poor soil water-holding capacity, low precipitation, unsuitable substrate, land use pressures, plant competition)	
14a. Valley fill does not undergo processes of aggradation and degradation	Valley fill, drainage depression
14b. Valley fill evolves through processes of aggradation and degradation	Cut and fill, discontinuous ephemeral stream
13b. Hydrologic and geomorphic conditions suitable for the development of herbaceous, hydrophytic, or swampy vegetation e.g. (high water holding capacity of soils, low stream power, perched water table, impervious subsoil, high periodicity of flow or runoff, sediment build-up)	
15a. Landform may or may not contain discontinuous pools	
16a. Landform may or may not undergo processes of aggradation and degradation	dell, swamp, mire, marsh, wetland, maya, wet meadow, swampy meadow, dambo, ciénegas
16b. Landform undergoes processes of aggradation and degradation	Cut and fill, discontinuous ephemeral stream
15b. Landform contains discontinuous pools, irregularly spaced and of variable size	Chain of ponds, beaver meadow
17a. Pools formed by beaver activity	Beaver meadow
17b. Pools formed by scour, sediment build-up or biological accumulation	Chain of ponds

development and exploitation outcomes. The status of a name is important, but this can be forged on watery ground when different interpretations can be given to the same system, as more knowledge is gained, or the system being named changes. Importantly, it has potential and significant ramifications in the legal jungle as the Six Mile Lake controversy attests. In this case, which is a landmark in American legal history (described in detail in 'Slide Mountain: the folly of owning nature; Steinberg, 1996) confusion as to what constitutes a lake or a river resulted in

a legal challenge between landholders and government that lasted for decades.

4.2.1. If swampy meadows were rivers

Moreover, in New South Wales, the *Rivers and Foreshores Improvement Act (NSW)* (1948) (referred to herein as the Act or the RFIA) makes provision for the remediation and protection of protected lands and protected waters, which includes, by virtue of the Act,

rivers and their associated banks (to a distance of 40 m) and beds.

The Act defines a 'river' as

...any stream of water, whether perennial or intermittent, flowing in a natural channel, or in a natural channel artificially improved, or in an artificial channel which has changed the course of the stream of water and any affluent, confluent, branch, or other stream into or from which the river flows...

This definition has led to many legal cases being contested in the High Court of Australia and the NSW Land and Environment Court as argued by Taylor and Stokes (2005). It is claimed that perennial and intermittent flows, as a determinate of a 'river', are not wholly characteristic of NSW rivers (a legacy of our English heritage) and as such provide legal loopholes for developers and landowners wishing to avoid the legal restrictions of river works imposed by the Act (Taylor and Stokes, 2005). If it can be deemed the drainage line is not hydrologically a river, then developers can pursue activities, such as engineering works and land development, without the need to obtain a Part 3A permit. This is more-or-less an Australian version of the Six Mile dispute.

So are swampy meadows protected within this Act? They are generally afforded protection from excavation, the removal of material or altering the flow of water by the NSW Department of Natural Resources (DNR), the department administering the RFIA, (Clayton Miller, personal communication, 2005). But this hangs loose on the very definition of a 'river' contained within the Act. (In practice though, due to limitations of resources, regional officers of the department may only assess developments in third order streams or higher. First and second order streams, which are known to contain swampy meadows, are generally not considered.)

Swampy meadows fail to be formally protected under this legislation for two main reasons. First, the RFIA river definition, in principle, is not inclusive of the intact swampy meadows as they are not channelised landforms so are not correctly defined as rivers. Secondly, DNR informally recognise rivers with channels (and hence protected water-courses) as those indicated by a blue line on 1:25,000 topographical map sheets and/or in catchment areas of less than 20 ha (Taylor and Stokes, 2005), thus excluding many upper catchment swampy meadow systems. These shades of grey can lead to confusion or potential legal implications. It may be a moot point, but when a swampy meadow is degraded with an incised channel, it can then be considered a 'river' and have the legislature in place to protect it. If on the other hand it is not degraded, but an intact swampy meadow, there is no legal provision for its protection—this being a swampy meadow conundrum.

4.2.2. If swampy meadows were recognised as wetlands

Currently in NSW there is no governance to specifically protect swampy meadows in the RFIA or the more recently

proclaimed *Water Management Act (NSW)* (2000). However, if they were more widely accepted as a wetland analogue there would be improved outcomes for their protection and conservation within governmental policy initiatives. For example, in the charter of the Wetlands Policy of the Commonwealth Government of Australia (Environment Australia, 1997), the NSW Wetlands Management Policy (DLWC, 1996) and the State Environmental Planning Policy No. 14—Coastal Wetlands (Parliamentary Counsel's Office, 2006), wetlands are to be conserved, managed and restored. Further, the NSW State Groundwater Dependent Ecosystems Policy (DLWC, 2002) makes provision for the recognition, protection and management of such systems; adding that Hatton and Evans (1998) have reported that there are many groundwater dependent or partially groundwater dependent wetland ecosystems in NSW. This also applies to the swampy meadow, where groundwater dependent ecosystems can vary from a state of non-existence to small, localised discharge areas, or to whole reaches.

Consideration of swampy meadows as a wetland analogue has additional implications. It would alter the perspectives of a natural-resource auditing process by improving the provisional status of wetlands. In the Central Tablelands of NSW, for example, the representation of wetlands is very poor. Reclaiming swampy meadows as wetlands would substantially improve this representation.

4.3. Restoration

Without a clear understanding of the ecological, hydrological and geomorphological characteristics and processes of a swampy meadow within a definitional framework, restoration goals are constrained within the perception and knowledge base of the land manager. For example, extensively incised and degraded swampy meadows altered to resemble dry valley fills, gullies or creeks may well be considered by the uninformed observer as natural landforms. Assigning incised swampy meadows with creek names can only validate the misconception. If the land manager's perception is that the degraded forms of the swampy meadow are in their natural and permanent state, then the restoration goals could be inappropriate, or there could be no apparent need for their restoration at all.

4.4. Land values

Swamps were thought to be home to trolls and water witches in traditional children's literature, a reflection of their low value (Moss, 1988). Swamps, including the swampy meadow, were considered useless, or harmful, unless drained for productive agriculture and disease control, their ecological and hydrological integrity being lost in the process. John Hughes (1878), an early settler in the Oberon district of NSW lamented that wealthy settlers '...are men who carve their own fortune and do not buy

bog and rock'. The poor image of swamps are changing as there is increasing recognition of their value as a *wetland* for flood control, sediment and nutrient retention and wildlife (Moss, 1988). Swampy meadows and their bad image also impact on the rural property market. In the NSW Central Tablelands, property agents have been quick to modify their terminology to serve a purpose. With increasing awareness of the effects of climate change and a greater reliance on permanent water for pastoral security, what was once disparagingly known as swamps are now more fashionably referred to as spring-fed gullies (D Crawford, personal communication, 2005). By virtue of this name change the swampy meadow becomes valued hydrologically, rather than devalued for its non-productiveness for grazing or cropping, or habitat for a life-stage of the parasitic liver fluke. The appropriation of a name, it seems, can help to determine conservation status of the swampy meadow and its land value.

5. Problems setting a definition

Construction of a swampy meadow definition has problems with scalar variables and user perspectives.

5.1. *Conflicting basis for a definition*

The basis for defining something is framed on the purpose for doing so. This can result in a number of definitions, leading to conflicts and confusion. Bullard and Nash (2000) discovered this when reviewing the classification of sand dunes in the Kalahari desert. Confusion and conflicts arose over the use of a variety of primary classification criteria, as well as differences in the underlying agendas for classification. Classification was also less than definitive due to the strong interdependency of many of the classification criteria. An additional problem was that few schemes encompassed the full range of dune types.

5.2. *Determining the definitional resolution*

The standpoint of the best resolution to define something has a lot to do with who is using it and for what purpose. For example, the generic term snow hardly reflects the 18 names given to snow in Inuit language (Pruitt, 1960). Similarly, the term 'dambo' has also had shifts in meaning. Originally used by local people of Zambia to indicate various kinds of seasonally wet grass-covered and treeless areas, and offering good pasturage to ungulates, this term did not distinguish between floodplain and valley floor systems. When scientists provided more precise definitions and terms, therefore becoming more specific, the scale changed and different types of dambos were able to be recognised across this particular landscape (Mäkel, 1974).

Each successive scalar or taxonomic reduction results in a more specific characterisation, and a change in definition. To illustrate, using an example given by Briggs (1981), a broad definition or characterisation of a swamp is inclusive

and defines what is common amongst the group. With increasing definitional resolution, the characterisation becomes more specific, distinguishing a swamp forest, swamp shrubland, swamp heath, swamp grassland, or a swamp herbland. With further reduction, the swamp grassland, for example, divides into wet grasslands, phragmites grasslands, typha grasslands, tussock grasslands and so on.

The problem, however, is defining a swampy meadow that is meaningful and transferable across countries, disciplines and user groups. Too specific a definition, and there is a risk of excluding a range of swampy meadow types, and too coarse a definition, the characterisation becomes meaningless.

5.3. *Spatial scale matters*

A swampy meadow is a large-scale system within which a number of processes and morphological characteristics can be present or absent at smaller scales. They are subcomponents of the system and interrelate with varying degrees of interdependency. At this smaller spatial scale, subcomponents are dynamic; responding to shifts in intrinsic or extrinsic influences and may be transient in time—so using these features as a landform determinate is problematic. Some of these subcomponents, singly or in combination, can include dry valley floors, fens, bogs, marshes, gullies and ponds, but also process driven zones, for example, areas of aggradation, incision, peat formation, anaerobiosis and sediment accumulation. Therefore as swampy meadows are system-based not component-based, one component should not be used to define the system: the large-scale characteristic of the landform is the determinant.

5.4. *When time is in question*

The problems with nomenclature and definitions get worse: they change with time. When is a swampy meadow a swampy meadow and when is it a gully or a creek? Iconic names such as, Chain of ponds Creek, Number One Swamp, Black Springs Creek, Macquarie Swamp and Mandurama Ponds are contemporary creeks marked on the NSW Mandurama 8734 topographical map. The terminology used in these names would suggest a different stream character prior to channel incision. This notion is supported by the fact that in the vicinity of these creeks and gullies, vestiges of swampy meadows are common along other drainage lines. Generally, swampy meadows are not noteworthy features on a topographical map (unless they cover a wide expanse and are generally flat and treeless), but once they become incised and degraded to a creek or gully they are identifiable on these maps by a blue line.

But what if these creeks, in time and with a significant change in boundary conditions, were reinstated as functioning swampy meadow systems? It is known that, in a natural system, there are distinct phases of aggradation and

degradation extending over variable lengths time periods; they readjust in the landscape to assume cyclically similar functions and morphology (Schumm et al., 1984; Renwick, 1992). Alternatively, in a degraded system with continuing disturbance regimes, the rate of degradation is always equal to, or greater than, the rate of recovery, and hence the system remains in a degraded, or gullied, state (Fryirs and Brierley, 2000) (Fig. 3). Therefore, basing a definition on how a system is observed at a particular snapshot in time does not really consider natural system changes. Further, it gives a strong case to the key concepts of time, management, and potential for change. In addition, reliance on physical attributes as a major contributor to swampy meadow characterisation can no longer service this system's identity. A better understanding of processes at a broad band of scales will aid in system clarification, classification and definition.

5.5. Construction of a definition

The principles used in the construction of a definition enable the swampy meadow to be differentiated from other landforms; be applicable across a range of scales; be inclusive of the many variable types; be capable of recognising specific evolutionary forms; and reflect a multidisciplinary approach when considering morphological and process-orientated characteristics.

Thus, a swampy meadow, as illustrated in Fig. 1, can be defined as

A low energy, valley fill landform system, without a continuous channel and with or without disconnected pools, but commonly with multiple flow pathways; able to modify local scale water flow dynamics; maintaining permanently or periodically saturated soils from surface water ponding or shallow groundwater thus enabling plant production to be maintained for varying periods under drought conditions; an accumulator of organic matter or peat; being dominated by hydrophytic herbaceous perennial grasses, sedges and rushes; a system which can exhibit phases of aggradation and incision, over a range of spatial and temporal scales.

This definition is dependent on managerial input. It puts no value judgement on the potential for the system to recover after degradation, as the potential to recover can be highly dependent on natural intrinsic or extrinsic factors, and external human resources of labour, on-ground works and materials. Its ability to recover may only be limited by time and resources. Further, the ability to deduce a degraded system as being a prior swampy meadow may require the use of a number of lines of historic and current evidence.

If the system is indeed incised and gullied, it may be purposeful to describe it as a 'gullied swampy meadow', or

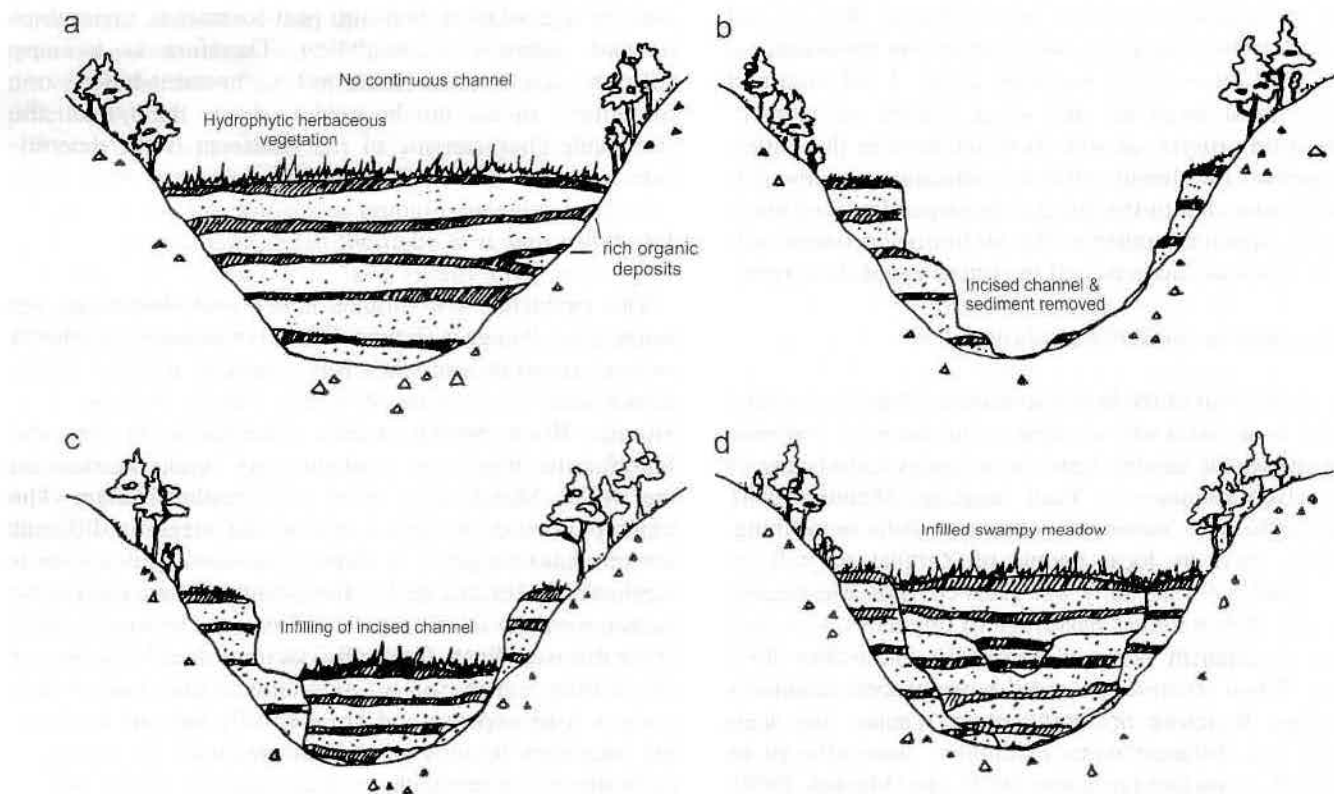


Fig. 3. Schematic diagram of a typical swampy meadow shows some characteristic features and the evolutionary phases of incision and aggradation. (a) Swampy meadow characterised by a discontinuous channel and hydrophytic herbaceous vegetation; (b) phase of incision; (c) phase of aggradation; and (d) progressive aggradation results in an infilled swampy meadow. The degradation of the swampy meadow from (a) to (b) can occur relatively rapidly whereas the formation of a mature swampy meadow under natural conditions is a very slow process.

if the system has both degraded and intact sections, it can be referred to as a 'multiple-stage swampy meadow'—thereby increasing its definitional resolution. There can be an initiation of many 'sub-definitions' describing a wide range of attributes such as: the swampy meadow during various stages in its evolution, the predominant vegetation type, and its topological setting and hydrological function, etc. The resolution of definition and the characterisations given to these is the governance of the user.

6. Conclusions

We have shown with our exploration of the swampy meadow conundrum that terminological uncertainty has repercussions for environmental, social and economic development. It restricts our ability to understand ecological, hydrological and geomorphological characteristics of the system across landscapes; hinders efforts to restore degraded systems and limits knowledge transfer between scientific disciplines. It also affects our ability to conserve or restore swampy meadow systems within specific legislative frameworks.

As our understanding of the swampy meadow grows, it is expected that definitions will also continue to evolve. As well, the resolution may become more specific in recognition of the many different types and evolutionary forms of swampy meadows in the landscape. This will eventually be transferred into legislative and policy frameworks, allowing for their listing in conservation legislation. We suggest that current policy makers, particularly in Australia, treat degraded swampy meadows which have turned into creeks and gullies as ephemeral rivers. As a conservation paradox, current government policy and legislation, instead of protecting natural waterways, including swampy meadows, only protects their degraded, channelised state.

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Management issues in a Tasmanian tourist cave: Potential microclimatic impacts of cave modifications

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Abstract

Caves can be difficult to navigate and often require physical modification to allow easy access for visitors. Single entrance caves double the access impact of each visitor. Visitors in tourist caves have direct physical effects such as the introduction of concrete and steel structures; transport of mud, dust, and nutrients; installation of lights and the exhalation of water vapour and carbon dioxide into the air. Indirect physical effects include alteration of the microclimate, both through physical modifications that change the ventilation regime and through the presence of visitors leading to changes in temperature, humidity and CO₂ within the cave environment. Anthropomorphic changes to cave physical environments to aid access or to reduce backtracking can have adverse effects on the internal microclimate of cave systems with subsequent changes to the cave environment affecting the quality of decorations and cave art and the diversity of cave fauna. Although often stated that caves operate at or near a constant temperature, closer examination indicates that cave temperatures are neither static nor constant. The degree of variation depends largely on the structure and physical characteristics of the cave. Air temperature and humidity gradients between the inside and outside cave environment can result in air density differences, which create airflow, which will in turn affect the cave microclimate. As part of the development of a management framework for King Solomons Cave, Tasmania, a study of the microclimate was carried out on behalf of Tasmanian Parks and Wildlife Service. Analysis of the variables showed significant differences in air temperature within each site and between sites. These differences range from 4 °C variation at one site to 0 °C at another site. The data were used to model potential airflow between the cave and the external environment. Results indicate that part of the cave is dominated by airflow between the chimney and the cave entrance leading to microclimatic fluctuations, while stable climatic conditions occur at the end of the cave. Future management strategies that propose a passage from the chamber to the surface via the current end zone would create a potential for airflow induced microclimatic change, leading to a change in both the temperature and moisture regimes, necessitating the construction of an airtight double door system.

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1. Introduction

Cave tourism offers an important source of both finance and educational opportunities for managers (Hamilton-Smith, 2004). However, visitors contribute extra fluxes of mass and energy into a usually stable low energy system that has developed under a regime of low rates of inputs. Caves can also be difficult to enter and navigate and often

require physical modification to allow easy access for visitors. These developments will in turn alter the fluxes of mass and energy resulting in departures from normal optimal conditions (Gillieson, 1996). These anthropomorphic changes have been shown to lead to a degradation of speleothems (Kermode, 1979; Atkins and Lee, 1993; Bunting, 1998), cave art (Aley, 2004) and ecosystems that have evolved to cope with relatively stable microclimate (Gillieson, 1996; Huppert et al., 1993).

The installation of concrete and steel walkways effect mass fluxes through the movement of water and nutrients (Gillieson, 1996; Michie, 2005). Visitors themselves also contribute to mass fluxes in tourist caves. Lint from

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clothing, skin flakes and hair, all accumulate in the cave environment and build up over time (Michie, 1999a). Bacteria and mud are introduced in the cave from shoes of tourists (and guides) and are splashed onto cave features (Bunting, 1998). The growth of algae and cyanobacteria near lights (lampenflora), change the appearance of cave features and the organic acids produced can potentially damage speleothems and cave paintings (Aley, 2004). Increased condensation from respiration has been shown to degrade speleothems (Sarbu and Lascu, 1997; Fernández-Cortés et al., 2006). Ammonia gas released in human breath and from the body is also a problem associated with the human impact on caves (Atkins and Lee, 1993).

One important impact of cave tourism that has received considerable study in recent years is the effect of increased CO₂ exhaled by cave visitors (e.g. Huppert et al., 1993; de Freitas and Banbury, 1999; Michie, 1999b; Eberhard et al., 2005). Levels of CO₂ above 2400 ppm can potentially lead to deterioration of speleothems (Kermode, 1979), while levels above 5000 ppm can be dangerous to humans. Where large numbers visit a cave system, adequate ventilation is required to prevent the build up of excessive CO₂ levels (de Freitas, 1998).

Visitors can also have considerable influence on energy fluxes into caves. Body heat from visitors and the output from lights contribute heat to the cave system (see Huppert et al., 1993; Gillieson, 1996 for a review). Kermode (1979) attributed 3.6% of temperature changes in the Waitomo Caves in NZ to the effects of people and lights. The breakdown of materials brought in by visitors also contributes to the energy input (Gillieson, 1996). Due to potential corrosion of gypsum crystals by condensation from visitors, a Geode in Pulpí, Spain was closed to visitors (Fernández-Cortés et al., 2006). In contrast to outside climatic conditions, caves generally exhibit relatively constant temperatures and high humidity. However, the microclimatic behaviour of caves is neither static nor constant (Wigley and Brown, 1976; de Freitas et al., 1982; Michie, 1984). Caves are very complex both structurally and environmentally resulting in a more differentiated environment between the outside and inside of a cave system. The cave environment can vary significantly, both temporally and spatially (e.g. Davies, 1969; Gamble et al., 2000; Jernigan and Swift, 2001; de Freitas et al., 1982). Significant microclimatic variations may occur within a specific section, or zone, as well as between those zones (Cropley, 1965; de Freitas et al., 1982). The degree of variation depends largely on the structure and physical characteristics of the cave with conditions becoming more stable with distance from entrances (Gillieson, 1996; de Freitas and Littlejohn, 1987). Multiple entrance caves have complicated microclimate conditions due to exchanges with the external environment via ventilation (e.g. Wigley and Brown, 1976; Bögli, 1980; de Freitas and Littlejohn, 1987).

The advection of heat and moisture into and from the cave system as a result of air movement has important

consequences for the cave microclimate (de Freitas and Littlejohn, 1987). As rock temperatures show little variation, condensation rates have been found to be primarily related to air exchange (de Freitas and Schmekal, 2003). During summer conditions, condensation is facilitated as the cave environment warms up, while evaporation occurs as cave air cools in winter conditions.

Caves with a single visitor access point require backtracking which effectively doubles the impact of each visitor, increasing pollution and the time that lights are left on. Fire hazards either from electrical lighting or above ground sources can also be life threatening for people trapped in single entrance caves. However, a number of tourist caves have experienced adverse changes to cave microclimate following physical modifications to open or widen entrances and passages (Lysenko, 1975; de Freitas and Banbury, 1999; Jernigan and Swift, 2001). The most significant change is augmented ventilation resulting in closer coupling with the external environment leading to increased fluctuations in temperature and humidity. This has been shown to have detrimental effects on cave vertebrates (Gillieson, 1996) and invertebrates (de Freitas and Banbury, 1999; Jernigan and Swift, 2001).

For example, increased air flow in the Glowworm Cave in NZ lead to adverse impacts on glow worms through the reduction in humidity and increased evaporation (de Freitas, 1998). However, closing an upper entrance in to reduce microclimatic fluctuations from increased ventilation resulted in elevated CO₂ concentrations. A structured plan of microclimate monitoring meant that a regime of door opening and closing dependant on outside conditions could be used to maintain conditions conducive to promote condensation while maintaining ventilation (de Freitas and Schmekal, 2003).

It is important that factors contributing to the cave microclimate are understood before any potential cave modifications are planned (Michie, 2005). In order to minimise visitor impact, cave managers need to determine the environmental management techniques that are appropriate to the particular cave conditions that occur in their particular cave system (Gillieson, 1996; de Freitas, 1998). The introduction of an appropriate monitoring system should assist cave managers to define and maintain an appropriate range of environmental conditions for their particular cave system (de Freitas, 1998).

1.1. Case study

King Solomons Cave, Mole Creek, Tasmania, is a small, but much decorated show cave with a high relictual value. In 1928, part of the cave was excavated to include an easier access and establish a new entrance. The cave is thus now a two-entrance cave, although the term “entrance” merely means another opening, and not necessarily a method for human passage. In this case, the original entrance more than 20 m above the pathway covered by a metal grate now functions as a chimney (Parks and Wildlife Service, 2004).

The entire route used by visitors is covered with a concrete pathway with concrete steps in steep sections.

The average number of visitors to the cave between 1992 and 2002 was 20,700/y with peak numbers occurring between December and April (Parks and Wildlife Service, 2004). There is evidence of ongoing pollution, probably due to congestion in some of the passageways of King Solomons Cave. A small portion of the cave, completely separated by a rock fall, known as Queen of Sheba Cave has a separate entrance. Cave management considered plans to initiate another excavation to join the caves, thus lowering traffic flow and ameliorating crowding and speleothem degradation by providing a one-way path as an alternative to backtracking (Parks and Wildlife Service, 2004).

Little is known about the effects of microclimate on cave flora in Tasmania (Eberhard, 2000). All fauna residing in State Reserve caves are protected under the *National Parks and Wildlife Act 1970*, and cannot be harmed or removed. The precautionary principle behoves managers to minimise potential impacts on cave microclimate that may adversely impact cave fauna.

In order to compare the benefits of reduced traffic against the potential impacts on cave speleothems and biodiversity due to modification of the cave microclimate from further excavation, a climate-monitoring program was set up at King Solomons Cave. This monitoring formed part of the “baseline data” stage instigated as a before–after control-impact (BACI) study examining the possible effects of excavation between King Solomons and Queen of Sheba Caves. Analysis of the resultant data can also be used to gain an understanding of the processes that control the microclimate of the cave system. This understanding of process can then be used to guide and inform assessment of the potential impacts of further changes. This paper presents the findings of this cave climate monitoring program, examines the processes that are contributing to the current cave microclimate and attempts to predict potential consequences to cave microclimate following further excavations to join the two caves.

2. Study site

King Solomons Cave is one of four show caves in Tasmania, and one of two show caves located in the Mole Creek Karst National Park. Mole Creek is located at the base of the Great Western Tiers at 41°33' south and 145°16' east. The Mole Creek area is characterised by well-jointed, dense, Ordovician limestones that are underlain by sandstones and conglomerates. Catchment for this area is mostly State Forest or private land developed for agriculture. Presently, Mole Creek can be classified as having a moist, cool, temperate climate (Fig. 1).

King Solomons Cave does not have an active stream and is considered a relict cave. Its source of water comes from a complex hydrological system that drains just west of the Cave. Minor east to west flows from underground

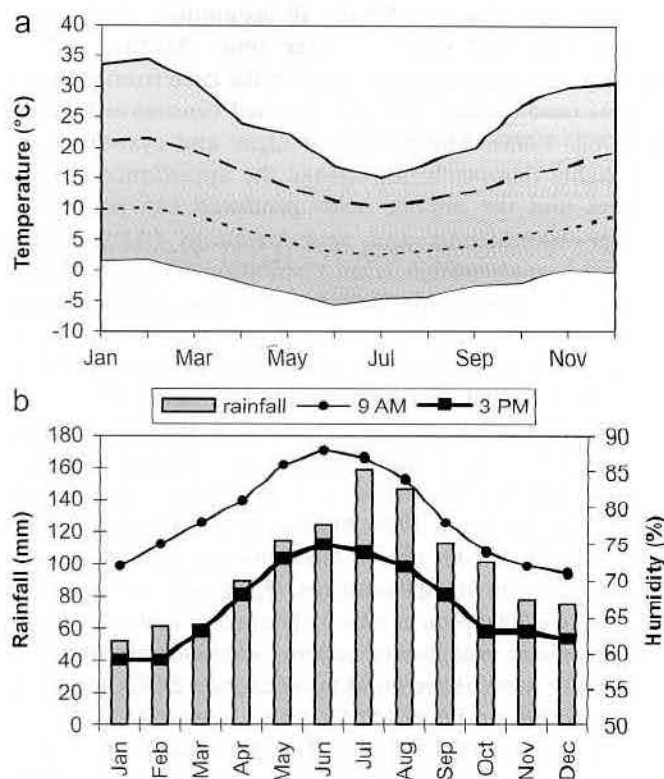


Fig. 1. (a) Highest daily maximum and minimum temperatures (grey), mean daily maximum (dashed line) and mean daily minimum (dotted line) for each month at Sheffield weather station (1906–2004). (b) Mean monthly rainfall (bars) and mean daily humidity at 9 AM and 3 PM for each month at the Sheffield weather station (1906–2004). Data provided by Australian Bureau of Meteorology.

percolation of rainfall on the slopes above the cave keep King Solomons Cave actively developing (Kiernan, 1990).

The layout of the cave is shown in Fig. 2. Prior to 1928, the original entrance to the cave was via a small sinkhole at the upper limit of the cave. This entrance, (Chimney) located at the southern end of a 0.5 ha grassy clearing within the surrounding Eucalypt forest, opens into a large chamber 8 m below the surface (Chamber) and is now covered by a metal grate. A blockage in a tunnel to the east of the Chamber was excavated in 1929 to restore a passageway (tunnel) to what is now the entrance to the cave (door), which is sealed with a metal door. From the chamber, the cave continues to the west until reaching an old rock fall (end). A small portion of the cave completely separated by the rockfall, has a separate entrance and is known as Queen of Sheba Cave.

Although no vertebrates live in Tasmanian caves, recent work in Tasmania shows that the biodiversity in Tasmanian caves is as robust as the warmer climates of the mainland although much of it is obscure from the untrained eye (Richardson et al., 1995). There are currently about seven identified species recorded for King Solomons Cave (Eberhard, 2000). Cave invertebrate fauna includes crickets, harvestmen, pseudoscorpions and beetles. The low numbers of cave crickets and spiders may be due to the

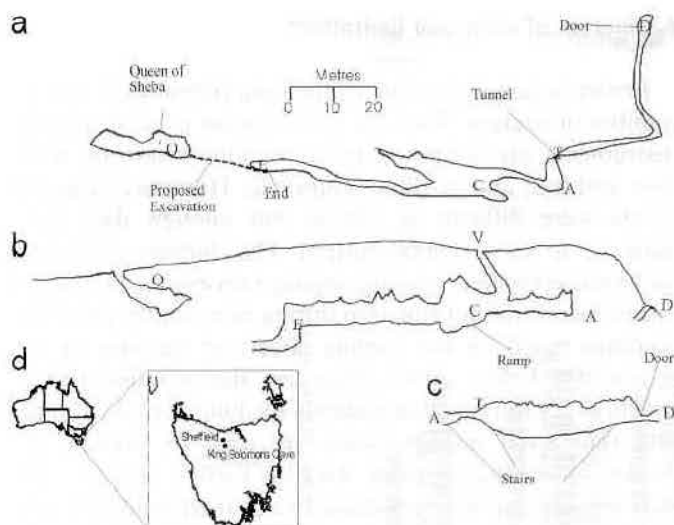


Fig. 2. (a) Plan view of King Solomons Cave and Queen of Sheba Caves. (b) Section of cave system from Q to A. (c) Section of the cave system from A to D. (d) The location of King Solomons Cave and the town of Sheffield the nearest weather station. The location of sampling sites are: (D) Kings Solomons door, (T) within the excavated tunnel, (C) within the chamber, (E) at the current end of the cave, and (Q) in Queen of Sheba Cave. (a) and (b) redrawn from original map by Joseph Wilks, District Surveyor, 1921.

solid entrance door. The observation of old spider webs may be an indication that *Hickmania troglodytes* were more abundant in King Solomons Cave (Eberhard, 2000).

3. Methods

Preliminary temperature measurements were carried out in July 2001 using three ACR JR auto logging thermistors (resolution 0.4°C , accuracy $\pm 0.2^{\circ}\text{C}$). The sensors were suspended from protrusions on the cave walls near the present entrance, King Solomons door (site D), within the chamber, which is below the chimney (site C), and at the current end of the cave (site E), see Fig. 2. Based on preliminary measurements, and taking into account the physical characteristics of the cave, five Vaisala HMP35 temperature (pt100, accuracy $\pm 0.3^{\circ}\text{C}$) and humidity probes (Humicap[®], accuracy $\pm 2\%$ at 0–90% RH, $\pm 3\%$ at 90–100% RH) connected to Data-i standalone data loggers were installed in the cave. The sensors were hung from protrusions on the cave walls so that they were located 1.5 m above the cave floor. The locations of the instruments as shown in Fig. 2 were: the present entrance, Kings Solomons door (site D), within the excavated tunnel (site T), within the chamber, (site C), at the current end of the cave (site E), and in Queen of Sheba Cave (site Q).

An outdoor weather station consisted of: a Vaisala HMP35 temperature/humidity probe in a radiation shield, a Met one cup anemometer and a Sensortech barometric pressure transducer. Two further pressure sensors were located at sites 3 and 5. The pressure sensors and the external weather sensors were connected to a Campbell CR10X data logger and data were averaged every 30 min. The collection period went from October

2001 to February 2002. A platinum resistance (hot-wire) anemometer was specially made to measure airflow at the mouth of the chimney. During calibration of this sensor, it was found that the poor signal to noise ratio meant that speeds of below 0.22 m/s could not be measured. This sensor was connected to the External Campbell logger between 20th January and 3rd February 2002.

4. Theoretical background

Previous research into cave microclimate has found that temperature variation is found to be greatest near the entrance and to decrease further into the cave (Copley, 1965; Wigley and Brown, 1976; de Freitas and Littlejohn, 1987). Water at different temperatures from streams (de Freitas and Littlejohn, 1987) and tidal flow (Gamble et al., 2000) can alter air temperatures. However, apart from heat conduction through the walls, outside influences are largely related to the advection of air into and within a cave (e.g. Davies, 1969; McLean, 1971; Michie, 1984).

Cave airflow is influenced by a number of processes. Cave *breathing* results from large synoptic driven barometric pressure differences between the inside and outside environment (Conn, 1966; Letheren, 1980). This effect is common in single entrance caves and is more pronounced in large volume caves. Stream flow can also drag an air current through a cave (Bögli, 1980). The most common cause of airflow is density differentials between air inside the cave and air outside the cave that are mainly a function of air temperature (de Freitas et al., 1982).

For the purpose of simplifying discussion we will use the convention of using seasonal descriptors to describe the relationship between air temperatures in the cave and the external environment. Summer (winter) conditions occur when the cave air temperature is lower (higher) than that of the external air.

In single entrance caves, exchange of air with the environment is controlled by the physical features of the cave (Cigna, 2004). Gravitational flow of cold air and return flow of displaced warm air has been found to occur under winter conditions in level single entrance sections of caves (de Freitas et al., 1982). Where the cave entrance is located near the top of the cave system, convective rising will occur in winter conditions but air circulation will be suppressed in summer conditions. If the surrounding topography is higher than the cave entrance, circulation will be enhanced by cold air drainage into a cave. Where a cave entrance is located at the bottom of a cave, cold air drainage in summer conditions will produce air flow (de Freitas et al., 1982), while winter conditions will suppress air circulation.

Several researchers have examined airflow and its effects within double entrance caves (e.g. de Freitas et al., 1982; Atkinson et al., 1983; Michie, 1984; de Freitas and Schmekel, 2003). While the rate and direction of airflow are still a response to the disequilibrium between the external air density and the cave air density, the actual flow

paths will be more complicated. Where one entrance is topographically lower than a second “chimney”, or vertical entrance, multiple entrance caves can produce a *chimney effect*. Under winter conditions, the warmer air of the cave will flow out of the chimney and be replaced by flow into the lower entrance. Under summer conditions, the cooler air of the cave will flow out of the lower entrance and be replaced with air from the chimney (de Freitas et al., 1982).

5. Calculation

Density differences between the cave and the external environment that drive airflow are due to differences in the density of the various constituents that make up the atmosphere at each site. These are influenced by the ambient temperature and the relative proportions of gaseous constituents particularly water vapour. Thus measurements of temperature and relative humidity differentiation between the inside and outside of the cave can be used to determine density difference and thus estimate potential airflow. From the predicted density differences, both the timing and direction of potential cave airflow can be determined.

The density of moist air is the sum of the density of its components: water vapour, and dry air (nitrogen 78%, oxygen 20.95%, argon 0.93% and carbon dioxide 0.03%) (Monteith and Unsworth, 1990). Using the ideal gas law, density (ρ) can be determined by

$$\rho = \{M_w e + M_a (P - e)\} / RT, \quad (1)$$

where M_w is the molecular weight of water in kg mol^{-1} , e the vapour pressure in Pa, M_a the molecular weight of air in kg mol^{-1} , P the pressure in Pa, R the universal gas constant— $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and T the temperature in K (Monteith and Unsworth, 1990).

Using a value of 0.029 for the molecular weight of dry air (Monteith and Unsworth, 1990) and substituting values for constants, Eq. (1) becomes

$$\rho = \{0.018e + 0.029(P - e)\} / (8.314T). \quad (2)$$

Relative humidity can be converted to vapour pressure (e) in kg m^{-3}

$$e = 0.01RH e^*, \quad (3)$$

where RH is the relative humidity and e^* the saturation vapour pressure at ambient temperature from published tables or equations (e.g. Murray, 1967; Monteith and Unsworth, 1990).

Measurements of temperature and humidity at the chamber site (3) and at the weather station were used to model atmospheric density in the interior of the cave ρ_{int} and for the exterior environment ρ_{ext} and differences were then calculated. The short period of wind measurements were used to verify the model results.

6. Sources of error and limitations

Errors occurred in some of the data periodically from a number of sources. The cave environment is harsh and the instruments are subjected to continuous moisture, mud, dust and lint, and possible tampering. Humidity measurements were difficult to obtain but enough data were gathered to see a general pattern. The chimney wind data had some erroneous readings during rain events. Hot-wired anemometers do not function during rain as they give false readings based on the cooling effects of the rain on the sensor (De Felice, 2000). They are also not designed to function in external environments for long periods of time, and thus wind measurements are used to validate the model, rather than provide data for further analysis. The data loggers that were purchased to be used inside the cave were not as robust as they were purported to be and outside instruments attached to the weather station were subject to animals chewing wires and interfering with the anemometer.

7. Results

7.1. Pressure

Regression equations between outside pressure and both Queen of Sheba and chamber sites showed very high correlations with r^2 -values of 0.9926 and 0.9866.

7.2. Temperature and humidity

Fig. 3 shows the mean and the standard deviations of the air temperature recorded for each site over the measurement period. The temperature varies almost 4°C between locations, with the highest average temperature being 11.5°C in King Solomons chamber, and the lowest average temperature being 9.2°C in Queen of Sheba. The most striking feature is that there is no variation in air

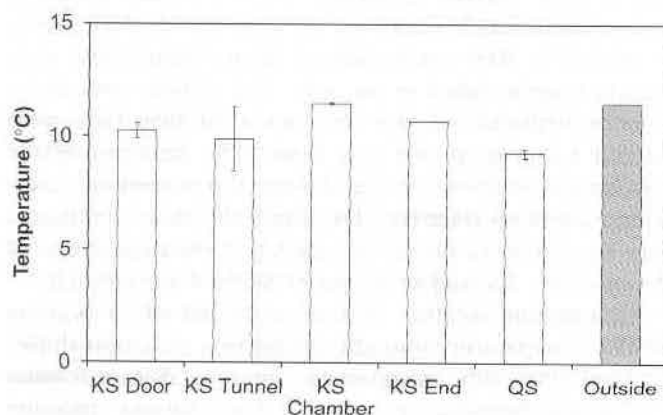


Fig. 3. The average air temperature recorded for each site within the cave. Error bars show the variance. Also the average air temperature at the external weather station above the cave is shown. Note error bars are not shown for this site.

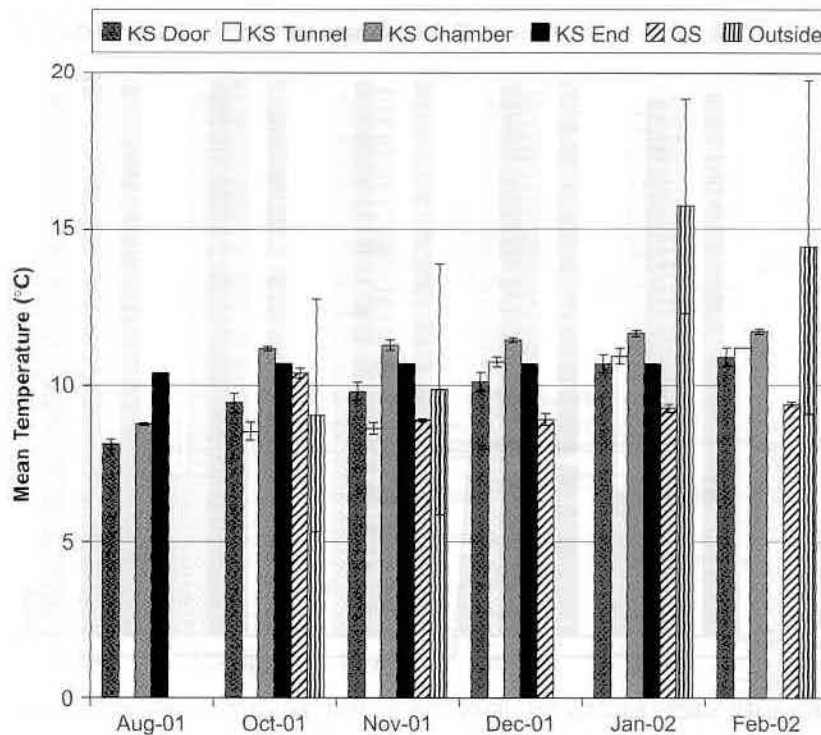


Fig. 4. Mean monthly air temperatures at each site over the study period. Error bars show standard deviation.

temperature at the end of the cave. Variation is minimal in the chamber and more obvious at the door. Despite the limited range of measurements, the tunnel site located between the upper and lower entrances shows the greatest variation.

Fig. 4 shows monthly mean air temperatures over the study period. King Solomons door shows an increase with time as outside temperatures increase. The tunnel is the coldest site in October and November but increases in temperature after this time and subsequently becomes warmer than all other sites except the chamber until measurements ceased in February. Queen of Sheba shows a drop in temperature between October and November.

Fig. 5 shows monthly mean humidity levels over the study period. Cave humidity levels are generally well above outside values. Within the cave, humidity tended to remain high at all sites and showed little variation. The tunnel site consistently showed the lowest humidity with the greatest variation. Queen of Sheba generally showed lower values than King Solomons and some variation, especially in October.

7.3. Wind speed

A comparison of measured cave wind with external wind did not show any correlation ($R^2 = 0.008$). A correlation ($R^2 = 0.52$) was found between wind speeds at the chimney and high temperature differentials between the internal chamber and the air temperature at the weather station.

Air temperature and humidity were used to predict potential airflow within King Solomons Cave using Eqs (2) and (3). The resultant calculated density differences are shown in Fig. 6. In the figure, positive density differences indicate potential airflow from the cave to the external environment, while negative values represent airflow into the cave. Values below the minimum STN are left in to distinguish periods where data were collected.

The modelled wind flow potential indicates that positive differences (external density greater than interior) occur more often and reach higher values than negative differences. Measured winds are stronger when potential airflow is from the cave to the exterior. Only occasional light wind occurs when the airflow potential is from the exterior into the cave. The relative strength of the modelled potential wind flow shows the same pattern as the measured wind, with times of high potential co-occurring with high measured wind speed. Cave winds were found to be strongest in the evening with peak flows around 15:00.

Detailed results of chimney wind speeds and the modelled potential wind flow over the course of two single days are shown in Fig. 7. The first day is a normal operating day, while the second is a public holiday when the cave was closed to visitors. The figure clearly indicates the influence of opening the cave door for tours on airflow through the cave. The measured flow at 14:00 coincides with the peak in temperature and humidity difference. The measured flow outside of tour times at 06:00, 08:00 and 18:00 on Tuesday, 29 January supports the occurrence of airflow even when the door is closed.

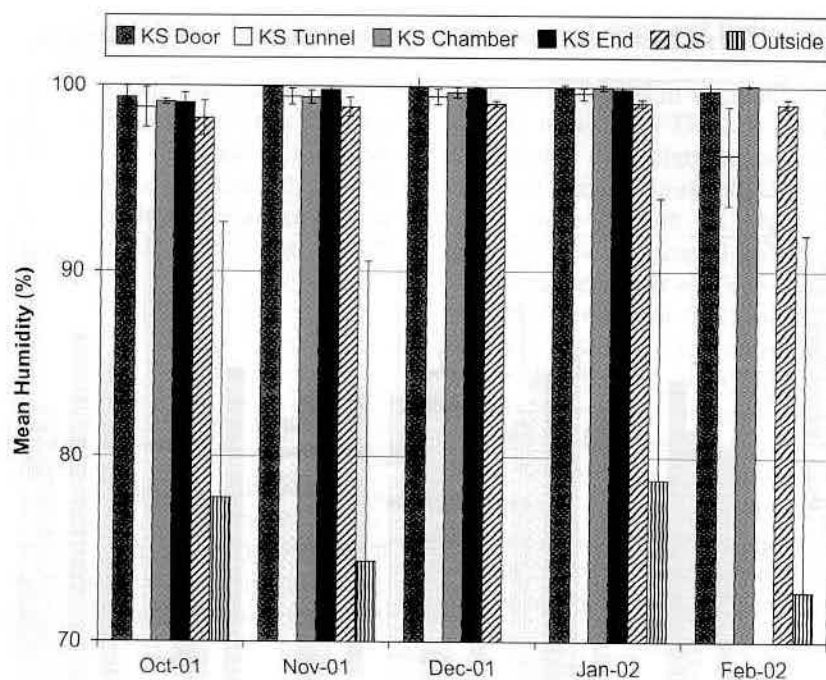


Fig. 5. Mean monthly relative humidity at each site over the study period. Error bars show standard deviation.

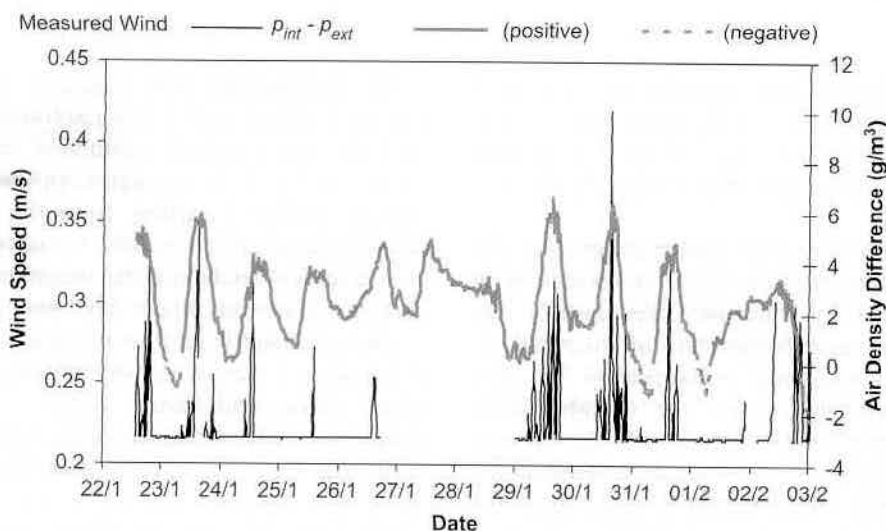


Fig. 6. Measured wind speeds at the chimney and modelled potential airflow based on temperature and humidity differences between the chamber and the outside weather station.

8. Discussion

The five sites sampled for temperature and humidity show a range of external influences. The chamber site (3), directly below the chimney and separated from the clearing on the surface by a relatively thin layer of limestone tends to show the highest air temperature. The end of the cave (4) is under a considerable layer of limestone and the stability of the temperature at this site indicates that it is isolated from external influences. This area of the cave can be

considered to operate as a deep cave zone. Air temperatures near the door to the present entrance (1) appear to be coupled to the outside, and as Fig. 3 shows, warm up as outside air temperatures increase in summer.

The microclimate of Queen of Sheba cave does show some variation but as it only has a single entrance the microclimate is controlled by different processes. The cave mouth is topographically higher than much of the rest of the cave and opens via a sink hole onto a south facing forested slope. Temperatures here appear to be influenced

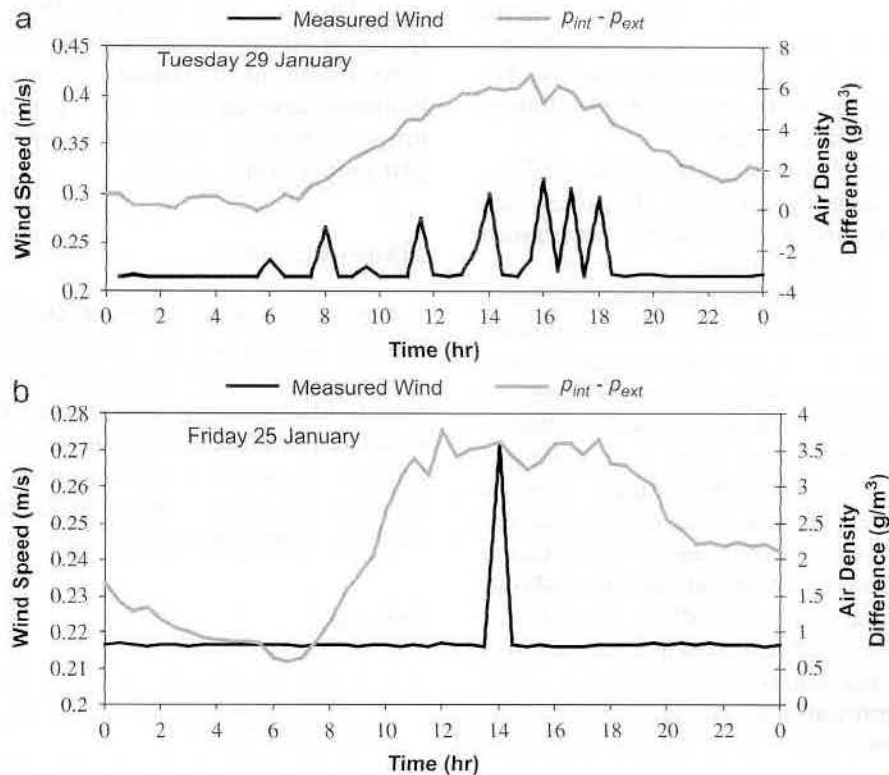


Fig. 7. Measured wind speeds at the chimney and modelled potential airflow based on temperature and humidity differences between the chamber and the outside weather station. For (a) Tuesday, 29 January and (b) Friday, 25 January.

by at least two factors, temperatures in the forest above reducing the external range, especially in summer, and cold air drainage from the slopes well above the entrance.

Variation in the microclimate at the tunnel site (2) is considered below in the light of the effects of the physical environment on airflow.

Both de Freitas et al. (1982) and Michie (1984), discuss reversal of the airflow regime due to the greater fluctuations of outside air density. Reversal effects should occur on both a diurnal and a seasonal basis. On a diurnal basis, reversal should occur in the evening when outside temperature tends to drop below cave temperature values, and in the morning when outside temperature rises above cave temperature. There would also be a reversal of flow on a seasonal basis as external temperatures become lower or higher than cave temperatures.

The potential model created for summer conditions in King Solomons Cave shows a potential for an airflow pattern predominantly in an outward wind direction due to greater density within the cave. The agreement of the model and measurements indicate a direct link between cave winds and density differences between the inside and outside environment. The greater measured flow when potential airflow is from the cave to the exterior indicates that cave winds are likely to be stronger in summer conditions than winter conditions.

The door to King Solomons Cave, while not completely airtight, is a relatively close fit. From analysis of airflow for single days, when the door is open for a tour, pressure

differences can be equalised and airflow occurs. When the door is closed the cave may be acting as a single entrance cave with little air movement until some threshold in density difference is reached, above which air flow occurs for a brief period.

The tunnel section of King Solomons Cave is narrow and constructed of rock fill, which is very different from the rest of the cave. Air flowing through the tunnel to equalise the density difference between the entrances, would increase in velocity due to the constriction of space, creating a Bernoulli effect. As the velocity increases, the friction from the walls and curvature of the tunnel would increase turbulence.

During cooler months, winds flowing from the outside into the cave would transport colder external air into the tunnel. During the warmer months from December to February, the modelled potential airflow direction is predominantly from the cave to the door. As outside air temperatures increase, the temperature of the air flowing through the cave would be expected to increase, which would in turn lead to an increase in tunnel temperatures. The combination of periodically increased evaporative potential, higher temperatures and the more unconsolidated sediments would contribute to the more variable and generally lower moisture regime at this site.

Despite the relatively short time frame of the measurement period, the results of this study indicate that parts of King Solomons Cave are dynamic, with a relatively high degree of variability in air temperature operating under the

effect of airflow between the cave and the external environment. Parts of the cave show temperature changes in response to variation in the direction of this airflow. The pattern of airflow is connected to opening of the door to allow tourist to enter the cave system.

The section of the cave that is currently the physical end of the cave is isolated from the effects of the airflow and operates as a deep cave zone. In this section, temperature and humidity exhibit very little change.

The relatively large variation in microclimate that is found at the tunnel site indicates that increased ventilation leads to greater fluctuations in humidity and temperature. Excavation of the fill between King Solomons Cave and Queen of Sheba Cave would result in increased ventilation, leading to a greater influence of the external environment. This would have the potential to dramatically alter the existing microclimatic regime that exists in both the end zone of King Solomons Cave and Queen of Sheba Cave.

As a result of the potential effects on cave invertebrates due to modification of the cave microclimate found by this study and on the basis of additional economic implications, the proposed plan for excavations to join the two caves was dropped. Instead, improved low voltage self-contained lighting, a boot washing station and stainless steel hand rails were installed.

9. Conclusion

Visitors in tourist caves have direct physical effects such as the introduction of concrete and steel structures; transport of mud, dust, and nutrients; installation of lights and the exhalation of water vapour and carbon dioxide into the air. Indirect physical effects include alteration of the microclimate, both through physical modifications that change the ventilation regime and through the presence of visitors leading to changes in temperature, humidity and CO₂ within the cave environment.

This climate study gives cave managers some ability to predict how physical modifications might affect the microclimate and hence what management arrangements should be put in place to maintain pre-existing conditions. It also provides data for comparison of before and after scenarios.

Despite the relatively short time frame of the measurement period, the results show that King Solomons Cave is made up of a number of zones, each with varying degrees of coupling to the external environment. The extent of this coupling can be related to the physical structure of the cave system.

Construction of a passage from the chamber to the surface via the current end zone would create a potential for airflow induced microclimatic change, leading to a change in both the temperature and moisture regimes. Any cave modifications must be carried out in the light of this information. Physical modifications to the cave must incorporate methods to stop the possibility of airflow changing the hydrological regime of the end zone of the

cave. This would necessitate at least a double door at the Queen of Sheba entrance and preferably airtight doors.

As a result of the potential changes in the microclimate following cave modifications identified in this study, the proposed plan for excavations were replaced with measures that reduce visitor impact.

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The economic value of water use: Implications for implementing the Water Framework Directive in Scotland

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Abstract

The European Union Water Framework Directive (WFD) enshrines several economic principles in pursuit of ‘good ecological status’ for Europe’s waters and rationalising water use in society. The implicit principle of maximising the social value from use of a scarce resource is reminiscent of the debate about treating water as an economic good, which has competing uses in society. This paper locates the debate about the economic value of water in the requirements of WFD. Specifically, we consider the implications of national reporting requirements for the economic characterisation report that stress the identification of relative value derived from use. As part of the Scottish contribution to the UK reporting exercise, we use a range of secondary data sources to derive economic values for water on a sector basis. We suggest whether the implications of different water values can be followed through in the WFD.

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Keywords: Water Framework Directive; Water valuation

1. Introduction

The Water Framework Directive (WFD) is possibly the most ambitious and far-reaching piece of environmental legislation to have originated from the European Union.¹ Its implications are at once simple and extremely far-reaching. The ultimate aim of the Directive is that water is sustainably managed at a river basin level and that water quality reaches good ecological status by 2015 (with extensions and less stringent objectives available). At the outset the Directive states “water is not a commercial product like any other but, rather, a heritage which must be protected, defended and treated as such”. This language conveys the spirit of sustaining a vital resource, but water supply is also an economic activity with public and private costs and benefits. This reality emerges later in the Directive, which goes on to incorporate a number of economic principles into the management of water in EU member states. These include the polluter pays principle,

approaches such as cost-effectiveness analysis of pollution mitigation measures, and consideration of economic instruments such as water pricing.

Water pricing policy relates to a further requirement to enact cost recovery. Consistent with the polluter and user pays principles, the Directive actually suggests that users should pay the full costs² of either extractive or discharge water use. By facing polluters with some combination of abatement and damage costs, the argument goes that they will be less inclined to over use the assimilative capacity of watercourses in an unsustainable way. The underlying aim here then, is the rationalisation of water use in member states and the drive to increase efficiency of resource use; in this case abstractive and discharge capacities. In simple terms this equates to the application of a basic economic principle of deriving maximum social benefit from allocations of a scarce resource. In the case of water this argument then suggests that water should—with understandable social safeguards—be treated as an economic good: societies should decide how to allocate water

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¹<http://forum.europa.eu.int/Public/irc/env/wfd>.

²Article 9, Paragraph 9.1.

between high and low value uses and if necessary water should be re allocated to its highest social value.

The pursuit of full cost recovery or pricing raises the question of which costs should be recovered from users. Specifically should the definition of *full cost* of use include the opportunity cost? That is, if a low value use precludes a higher value use, then social welfare is not maximised without some form of resource transfer. This interpretation has sound economic logic but presents practical difficulties in terms of pre existing rights and the absence of water markets to facilitate the transfer.

This paper explores issue of water valuation and the broader context of treating water as an economic good. It does so in relation to the implementation of the WFD, and more specifically the reporting requirements of the Economic Characterisation report as required in the implementation timetable. The Characterisation is an early reporting requirement of all implementing member states.³

The next section scrutinises the economic interpretations and spells out what this actually implies in terms of the need to determine the economic value of water use. The following section then undertakes a review of the value of water in different sectors of Scottish industry. The results highlight a number of problems associated with the different approaches to determine the social value of water use. More broadly the clarification of the economic concept of value is often at odds with how industries perceive the significance of their own use. The final section draws some conclusions regarding the value of this economic information and the institutional requirements for the implementation of efficient water use.

2. Background

The WFD refers to good water quality⁴ and an objective for Member States to achieve “good surface water status” and “good groundwater status”, and prevent deterioration in the quality of waters, which are already “good”. To achieve this, member states are required to develop river basin level intervention programmes based on the most cost-effective measures that are technically feasible and not disproportionately expensive. The latter is vaguely defined in terms of the broad social costs that might accrue to the spectrum of stakeholders within a basin. Economic instruments, including pricing policy, should be considered and there should be specific attempts to allocate costs to polluters. All this is to be delivered using some form of participatory approach to maximise stakeholder buy-in.

The early economic reporting requirement for compliance attempts to collect basic economic information about who uses water, and the values they derive from use. This

in turn raises questions about the definition of uses and the nature of any costs, specifically environmental and resource costs, associated with different uses. In defining these elements considerable weight is given to economic definitions that can be translated into monetary values. Implicitly the ability to measure these impacts provides a basis for recovery charging and other instruments.

Amongst economic experts, the interpretation of this directive has varied and early guidelines⁵ were confusing. It is interesting to note that the reference to ‘environmental and natural resource costs’ is omitted from Annex III which merely refers to ‘principle of recovery of costs of water services’. However, this apparent clarification does not completely simplify the process of determining the significance of the different forms of use and costs associated with different uses.

3. Exploring use, value and cost

Water is also used for a variety of human purposes, from which people derive a range of values. Some of these use categories are summarised in Fig. 1.

The WFD is explicitly concerned with use values, both direct and indirect. Direct value can derive through inclusion in products such as drinks, as a medium for growth for aquaculture, for cooling of industrial facilities, or as a carrier for discharges. These uses are mainly extractive and consumptive. Indirect includes recreational and aesthetic uses. These are typically non-extractive and non-consumptive. Some uses under the “other” category in Fig. 1 can also be classed as non-use in the sense of being associated with optional, bequest or existence value. These categories are associated with water left in situ and in good ecological condition. It should be noted, however, that some texts on the Directive have used the term non-use to indicate non-abstractive use (e.g. hydropower), as opposed to a passive activity totally unrelated to any direct exploitation.

Overall, there is considerable scope for differences of opinion about the notion of use. For example, whether the use is in-stream or not, does not necessarily indicate the use to which water is put, or the impacts on the water. Some abstraction and discharge may occur with little difference between the time and place of abstraction and that of discharge, and with little change to the quality of the water. On the other hand, there may be significant changes. Similarly, in-stream uses can exhibit important variations. Use can be determined differently, and generally consists of a number of different aspects, for example use by an industry for cooling, as part of their product, for domestic purposes, etc. This is an indication of the versatility and importance of water use, although it adds complications to attempts at comparable valuations.

³This requirement was supposed to be fulfilled by December 2004. The report collects necessary economic information on water use, economic significance and value to stakeholders.

⁴What is referred to as good status is then described in Annex V of the Directive.

⁵See for example details issued by the Common Implementation Strategy: Eco2 (WATECO): <<http://forum.europa.eu.int/Public/irc/env/wfd/library>>.

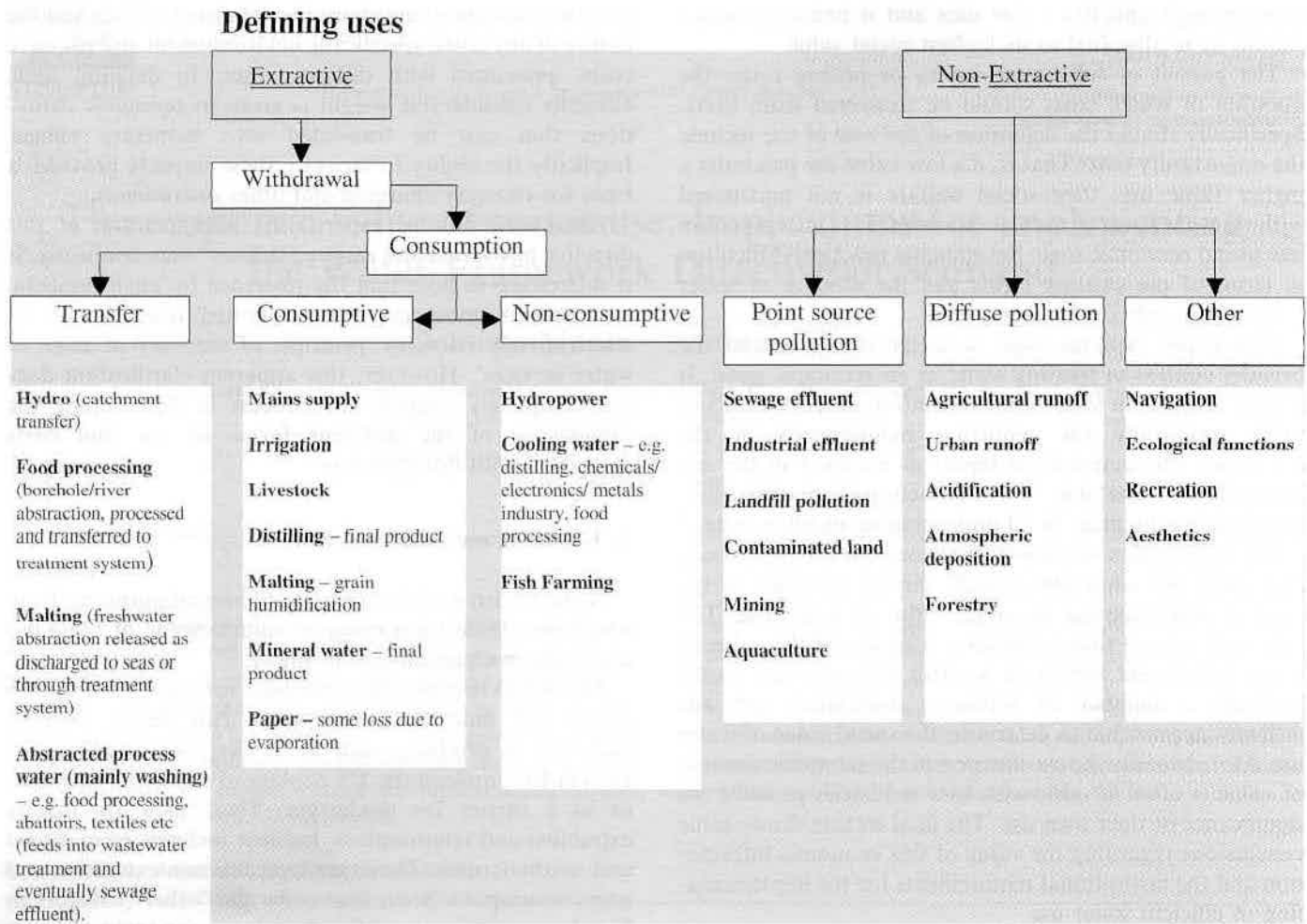


Fig. 1. Defining uses.

But as an adjunct to use and value derived, many users also incur costs. These include some that are not actually borne by themselves; so-called externalities. The first cost for many users is private cost of supply/dischage. In the case of supply, financial costs are conventionally collected for the calculation of long run marginal cost or its simplified equivalent Average Incremental Cost (OECD, 1987). Charges aligned with the financial cost of supply (capital, operation and maintenance) may be the ultimate aim of cost recovery, but charges based only on financial costs are unlikely to bring about a socially optimal water use. This is because a number of external costs remain. While users do not face these, then economists suggest that water use patterns are inefficient.

Accordingly the interpretation of “full” cost in Article 9 requires the consideration of several other relevant cost categories to consider; notably environmental and resource costs. Environmental costs are the marginal external costs associated with environmental damages arising from supply or discharge. They can arise as a result of extraction (low flow) and discharge. Methods used to calculate these costs and instruments used to factor them into user charges

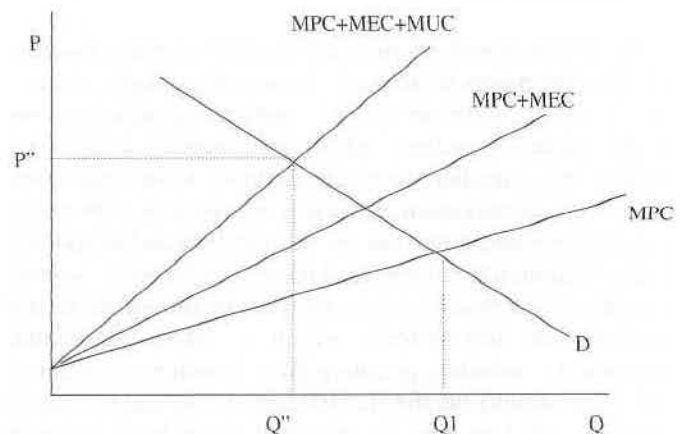


Fig. 2. Reduction in consumption when faced with economic and utility costs.

have exercised environmental economists for the last two decades (Hanley and Spash, 1993).

Fig. 2 shows these costs in a rudimentary economic diagram that relates water quantity consumption (x-axis) and cost (y-axis). The diagram then distinguishes the marginal private costs (or supply) schedule (MPC) from

the schedules that include further external (MEC) and user costs (MUC). In theory if users were faced with the total extra costs of consumption, then the optimal consumption level Q'' would be something less than that prevailing as a result of charging to recover financial costs only $Q1$.

The notion of a resource cost introduces further cost categories that require further clarification and interpretation. Within the concept of a resource cost, it is possible to identify the economic notions of user cost and opportunity cost. However, it is unclear what the guidance actually refers to and this has implications for the full cost recovery. The marginal user cost is the cost associated with future scarcity arising due to current consumption or quality depletion. This is an intergenerational concept arising from the future scarcity of a depletable resource. To all intents and purposes this is hard to implement. For all practical purposes it is unlikely that the true resource or user cost⁶ of supply can be consistently calculated because among other things it depends on the future costs of a replacement technology.

But documentation also suggests that a correct definition of resource cost should encompass any implicit opportunity cost of use. The notion of an opportunity cost is rudimentary yet powerful. The implication is that if there is a higher aggregate welfare (to society) gains from reallocating water between low- and high-value users. Put another way, not all current uses of water offer the best social return. This definition draws on an important economic principle of equi-marginal returns: for an efficient allocation of water between users, we require that the marginal values of water be the same between different users and equal to the marginal cost of supply. This principle is the main reason to seek out competing use values as a first step in determining the social value of alternative uses.

4. Valuation of water use in the UK

The economic theory of value offers a relatively unambiguous interpretation of the environmental and resource costs stated in the Directive. But the conclusions are both politically complex and (for certain users) unpalatable. Much recent debate about economic interpretations has foundered on the notion of value. Accordingly, the UK characterisation report has been undertaken in two different ways, with England and Wales adopting a different approach to that taken in Scotland and Northern Ireland.

In England and Wales the value of water use has been assessed by comparing the contribution of different sectors to the economy (in terms of gross value added) to their consumption of water. This approach has advantages in being relatively straightforward where good estimates of volume are available, and generally requiring less information than is necessary for the valuation using stricter

economic principles. Additionally, the approach accords with the view of some industrial stakeholders in Scotland who have contested the strict economic approach⁷ holding that value should be self evident if the user is a vital industry, e.g. energy or food production.

Whatever the interpretation of value, the Directive sets an obligation for member states to understand who uses water and what value they derive. On this basis the remainder of this paper derives economic values for sectors in the Scottish economy. This exercise gives some clues about the relative value assigned to water, which can be inform decisions taken to steer an economy towards socially beneficial patterns of use.

The uses we value are not necessarily dictated by a ranking of absolute value derived. We focus on sectors with available information on volume, social importance and applicability of a valuation technique. With reference to Fig. 1 we are interested in values associated with different forms of use value, whether associated with abstraction and discharge or in-stream use.

5. Valuation in Scotland

The economic valuation for Scotland adopts a variety of approaches used in the literature; see Gibbons (1986), Pearce (1999) and Renzetti (2002). The choice of methods is dictated primarily by the availability of basis data on revealed values or willingness to pay of water services.

Broadly speaking, it is important to distinguish between methods that use market (price) information to estimate value and those for which no market (price) information is available. In the former case, information is available from sales and purchase decisions. In the latter case there are no observable markets for specific water uses and therefore hypothetical or alternative markets must be used to gain an insight into a non-market value.

It is also important to specify whether values we derive are average or marginal values. Consistent with the principle of equi-marginal returns, some of the methods estimate the marginal value of water use. Although this is the most useful estimate of value from an economic point of view, it is also the most difficult to assess, and therefore only a small number of data intensive methods are available for this. Alternatively, some methods estimate total willingness to pay for the quantity of water consumed, and divide this by the quantity to approximate an average value.

Finally, the methods may differ in the type of water use that they value. As discussed in earlier sections, each sector or organisation is likely to use water in a number of different ways. For example, they may be supplied with domestic water for their staff, they may use water as part of their product or as a medium for transport or for cooling,

⁶See Warford (1994).

⁷The Scottish Environmental Protection Agency (SEPA) has subjected its preparatory work to scrutiny by stakeholder forums comprised of principal water users from industry.

and they may use water to discharge effluent. Each of these types of use will have a different value, depending on the opportunity to reduce or substitute water use and the contribution that water makes to economic output. Accordingly a method may estimate the value for one type of use, this may not be the total value to the user. Alternatively, a value for a particular user is likely to encompass a variety of values for uses within that sector. Some of the methods below are more applicable to valuing water use by sector while others are more relevant to valuing a use within a sector.

Appendix A, Table A1 summarises the broad categories of valuation method. This study draws on the range of methods to derive values using existing data and willingness to pay estimates derived from other studies on water demand.

5.1. Household use

Households receive a range of services from water, including the supply of clean water and the discharge of effluent.

Most consumers do not choose between a range of water services at different prices, but pay the rate determined by the local water authority: they are pay the single price that is typically estimated to represent the average cost of supply for domestic use. Therefore, the only way to measure the marginal value of water to the individual consumer is through the use of water demand functions. The slope of the demand curve is estimated by considering a one unit increase in water supply. The willingness to pay (WTP) for this increase in water supply use is estimated using the following the formula (Gibbons, 1986, p. 17):

$$GWTP = \left(\frac{P \cdot Q_2^x}{1-x} \right) \cdot \left(\frac{Q_2}{Q_2^x} - \frac{Q_1}{Q_1^x} \right),$$

where GWTP is gross willingness to pay, P is the price, Q_1 is the quantity consumed, Q_2 is the new quantity, and $x = 1/e$ where e is the elasticity of demand (independent of sign).

For application of the formula we need:

- consumption in Ml/year/per capita;
- price per Ml measured volumetric rate; and
- an elasticity of demand. Hoglund (1997) provides an estimate of -0.2 , from Swedish data that are transferable to Scottish consumers.

Per capita consumption in Scotland is estimated to be 143.3 l/day, or 52.3 Ml/year (Environment Agency, 2001a). The cost of consumption is estimated using the charge levied by Scottish Water for those households charged by volume. The costs paid by a consumer cover both supply of clean water and discharge of foul water, with the volume discharged estimated at 95% of the volume supplied. Therefore, the household faces a cost per megalitre that is a combination of the two charges. Scottish Water charges

those households charged by volume 67 p/Ml for clean water supply and 110 p/Ml for discharge of foul water (Scottish Water, 2003). Therefore, the effective charge for water services is 171.5 p/Ml supplied ($67 \text{ p} + (0.95 \times 110 \text{ p})$). Using this combination of prices requires us to assume that the elasticity of demand for supply and discharge of water is the same. Substituting these figures into the equation for gross willingness to pay generates an estimated value of 164 p/Ml (0.164 p/m^3).

It is also possible to consider a wider range of values obtained from different prices for water supply. Based on a combination of charges for supply and discharge as above, the charges made by the major water companies in England and Wales indicate a range of prices from 107.15 p/Ml (for Northumbrian Water) to 255.59 p/Ml (for South West Water). Substituting these prices into the formula for willingness to pay generates a range of values from 102.25 to 243.90 p/Ml ($0.102\text{--}0.244 \text{ p/m}^3$).

5.1.1. Household demand: stated preference approach

A different approach is to conduct a stated preference survey whereby customers are asked to indicate their willingness to pay for an improvement in service. The UK water regulatory agency conducted such a survey, though unfortunately the sample chosen was not random (Bolt, 1993). Out of the three kinds of service improvement, one related to reductions in the risk of supply interruptions. Households were willing to pay £28.8–32.7 per annum for this benefit. In 1997 price terms this is £32.40–36.80, or 48.6–55 ecu per household per year. Given an average consumption in England and Wales of about 54 Ml year, this is equivalent to 1 ecu/Ml, or £0.67/Ml (0.067 p/m^3). This is significantly lower than the estimate for value using Gibbons' willingness to pay formula. This is because the results using Gibbons' formula indicate the value of the supply of clean water and discharge of dirty water. In contrast, this stated preference survey considered clean water only.

If the value of household water use is considered for supply only, rather than for supply and discharge, the value falls from that calculated using Gibbon's formula above. This allows a more direct comparison with the results of the study undertaken by Bolt (1993) using a stated preference approach.

For Scotland, if price is taken to be 67 p/Ml of clean water supplied (instead of 171.5 p/Ml to include the charge for discharge of 95% of water supplied), the value calculated using the Gibbon's willingness to pay formula is calculated as 63.9 p/Ml. Using the range of costs for water supply for the water companies, the value of water use ranges from 54.8 to 86.4 p/Ml.

5.2. Agricultural irrigation

Agriculture relies on water for a variety of purposes, although this is largely provided by precipitation, with some additional irrigation of arable and horticultural

crops. Because of the costs associated with irrigation, this is generally limited to improving the yield and quality of high value crops such as potatoes, field vegetables and soft fruits, and is particularly important during summer periods of low rainfall. Water is also used by farmers for livestock watering and for cleaning equipment. The valuation undertaken in this paper is restricted to irrigation of potatoes a typically water use in Eastern Scotland.

For the profit-maximising farmer, demand for irrigation water is dependent on the following components:

- area of irrigated crop;
- availability of natural soil moisture from rain and dependent on evaporative demand;
- crop yield; and
- crop price (Environment Agency, 2001b).

These factors increase or reduce total irrigation water requirement year-to-year in order to generate a constant level of yield or quality. High crop yields may decrease the price one year, causing reduced crop areas in the next as farmers respond to lowered prices. However for the estimation of willingness to pay within one year, the most influential factors on demand, once a farmer has decided his total crop area, are climatic conditions that dictate how a farmer responds to day-to-day water needs.

We use net-back analysis as a method to derive a bound on farmer willingness to pay for water. The analysis calculates the maximum ability to pay for water use from the price of farm output less other farm costs. This allows calculation of the value of all water, including both irrigation water and naturally available water, as either pounds per hectare or pounds per tonne. The net-back value is calculated as follows (Bate and Dubourg, 1997):

$$\text{value} = (P_f \times Q_f) - C_{\text{non-w}},$$

where P_f is the market clearing price of the farm's output, Q_f is the quantity of the farm's output, and $C_{\text{non-w}}$ is the farm's total non-water costs of producing quantity Q_f .

To apply the method to agricultural irrigation, it is necessary to have data on the costs associated with irrigation, yield and revenues. The only crop for which this information is currently available is for potatoes. This data comes from a survey of farmers (SAC, 2001a, b; Scottish Executive Environment and Rural Affairs Department (SEERAD), 2002) looking at farms with irrigated potato crops in the West Pfeffer and Tyne catchments in Scotland. Although individual responses were confidential, the study reported aggregate statistics that can be used to calculate an average willingness to pay per hectare within the relevant catchments. These calculations are shown in Appendix B.

These calculations find net-back values for water used for irrigation of potatoes ranging between £200 and £894 l/ha, with a mean value of £5128/ha. The value varies with potato prices and yield. However, it should be noted that since netback values are based on the difference

between revenue and costs, they tend to represent a maximum value.

This study was necessarily location-specific due the lack of national statistics on location-specific irrigation water use and reliance on SEERAD (2002) data. However, the variation of scenarios presented in SEERAD (2002) allowed for a relatively broad consideration of demand under varying climatic condition. This makes the average results more representative than a static analysis of average moisture availability.

Since net-back analysis considers both irrigation and naturally available water, it is not possible to calculate a value of irrigation water per cubic metre using this method. However, it is possible to extend the method to focus on irrigation water by comparing yields with and without irrigation. Irrigation can be expected to affect yield of the crop of potatoes, and may also affect the price by reducing the quality of the produce. In a small data set from a farm trial in Cambridgeshire, the fully irrigated crop yielded between 14.3% and 58.1% higher than the unirrigated crop (depending on variety). Based on these figures and assuming no price effect, the value of water for irrigation is between £0.23 and £1.38/m³. However, these estimates are simplistic in not considering costs of abstraction licences or potato subsidies in England and the higher demand for irrigation water due to lower rainfall.

A simple net-back analysis of potato production across Scotland using national data for price, yield and hectares grown shows great variation in net-back figures, with some negative values. In addition, the average value per tonne produced was significantly lower than that calculated for the West Pfeffer catchment, although it was not possible to calculate a comparable value per cubic metre of water used because there was no data on total water used for irrigation of potatoes across Scotland. The analysis focused on mainware potato production (excluding potatoes for seed and stock feed) since the majority of irrigation is focused on this crop to enhance quality, yield and price (Scottish Executive, 2002). Because irrigation data for potatoes was not available, the national level analysis should be taken as indicative only. The lower value for Scotland as a whole is in large part a reflection of the lower yields per hectare and associated lower revenue. Since irrigation costs are largely determined by costs of equipment, which does not vary significantly, the lower profit margins reduce the net-back value. This suggests that the values found in the study of the West Pfeffer catchment could be higher than those for Scotland as a whole.

5.3. Aquaculture

Aquaculture is an economically important industry in rural Scotland and technically a high volume user of water. Water is used in aquaculture for a number of processes, including provision of oxygen, disposal of solid waste and nitrogen, and as a medium for growth. There are a number of potential methods to value the use of water for

aquaculture, including net-back analysis, cost of damages through water use and calculation of the private benefits. The calculations in this section focus on avoided costs for disposal of solid waste, since this was the only information available at the time of writing the report (Slaski, 2004, pers.comm.).

An alternative to disposal of solid waste in water is to remove it from the effluent stream before discharge by applying settlement or filtration techniques. To meet the conditions associated with discharge consents, some of these are used in fish farms already. Other technically feasible options such as recirculation systems are not financially viable at present. This section considers the costs of applying a standard drum filter technique to the volume of water abstracted to arrive at an estimate of avoided cost (Slaski, 2004, pers.comm.).

The report on abstraction in Scotland (CJC, 2002) estimated that aquaculture abstracted 4.4 million m³ each day. Effluent polishing recommendations from the main supplier of such filters (Hydrotech) suggest that 729 of their largest units (model 2007) would be required to treat this volume of discharge. Assuming that the filters are bought without a loan, there are two ongoing cost elements to using such filters, depreciation for having purchased and installed the filters, and electrical energy used to run them. Summing these two elements of running cost, the avoided cost for solids removal in abstracted aquaculture water is 0.126 p/m³.

This method results in a basic value for water use based on costs avoided by not removing effluent. However, there are a number of potential omissions from the calculations, which should be considered in further analysis. In particular, the value is based on all abstraction being able to use the largest filters, which may be associated with lower costs per unit volume of water than smaller filters. It also does not include extra time or costs associated with maintenance and cleaning of the filters, and it assumes that the filters are 100% efficient.

5.4. Salmon angling

The value of recreation, including angling, cannot be estimated using productivity approaches, but instead relies on methods to value non-market benefits. In addition, it is only possible to value the activity that uses water, without an estimate of value per cubic metre.

One appropriate method is the travel cost method, which considers the costs that an individual faces in travelling to the site. In the case of angling, one recent estimate of the value of angling to those taking part (rather than to the economy as a whole) was undertaken for salmon angling at a site in Co. Donegal, Republic of Ireland (Curtis, 2002). We assume that the values found in this study would be broadly transferable to Scotland since all of these countries have a good reputation for salmon fishing in particular rivers, and serve both local anglers and international visitors.

This paper found that the travel cost of the anglers surveyed was IR£68 (£58), of which IR£22 (£19) corresponded to travel costs, IR£14 (£12) were fishing expenses, and IR£32 (£27) was for accommodation and meals. However, the costs varied between different nationalities. Germans and other Europeans spent an average of IR£56 (£48) per day on accommodation and meals, and IR£58 (£49) per day on travel. Anglers from Northern Ireland spent the most on fishing expenses.

The value of angling also includes the consumer surplus. This is the value that is bounded by the true trip demand curve and is the additional value that an angler would be willing to pay over and above what he already pays. Consumer surplus can be derived from revealed (i.e. travel cost) or stated preference (contingent valuation) exercises.

The largest consumer surplus estimates were for non-Irish and older anglers, although the estimates did not vary much (from IR£115.6 to IR£161.5, or approximately £98–137). These estimates appear high relative to other published data (e.g. Toivonen et al., 2000) that suggests that consumer surplus represents a further 40% additional to travel costs. Total value of salmon angling is calculated by combining the estimates of travel costs and consumer surplus. This suggests a total willingness to pay of approximately £95 per day. The values for different nationalities surveyed are summarised in Table 1 (Curtis, 2002).

5.5. Industrial use

Because of the complexity of many industrial processes using water, the most realistic method for valuing industrial water use is the marginal productivity approach. Although this approach is the most data intensive, it allows most comprehensive inclusion of information on the costs of other inputs to production. However, estimating the marginal product of water to industry tends to be difficult because of (a) the low value that water tends to have relative to overall industrial costs of production and (b) the fact that actual water intake is less than gross water use. The difference between actual and gross intake arises because of the use of recirculating water, which can be substantial in contexts where the purity of water is not the highest concern. Maximum willingness to pay for water

Table 1
Mean travel costs and consumer surplus for anglers in Co. Donegal, IRE

IR£	Travel costs	Consumer surplus	Total mean willingness to pay
Northern Ireland	38.3	115.6	153.9
Republic of Ireland	48.8	145.9	194.7
Germany	132.6	161.5	294.1
Other European countries	117.6	151.7	269.3
Mean across countries	68	138.6	IR£206

therefore tends to approximate the marginal costs of treatment and re-use of water, or of alternative technologies that conserve water.

Unfortunately there is not sufficient data on firms' water use and non-water costs to be able to apply the model to Scotland or Northern Ireland. Therefore, it is necessary to rely on estimates made in a paper assessing the value of water use for Canadian industry (Renzetti and Dupont, 2003) and transfer the values to Scotland and Northern Ireland.

The paper by Renzetti and Dupont (2003) uses a cost minimisation function, which assumes that firms choose their inputs to production, including water, in order to minimise costs. These choices are made subject to the output to be produced and the fixed level of inputs that are not variable in the short run. Considering the problem another way, instead of minimising cost subject to a given production, a firm can maximise production subject to a constraint on cost. This way round, the production function indicates the relationship between output and inputs, including water. It is this relationship between output and the water input, with other inputs held constant, that determines a shadow price or unit willingness to pay for water based on the change in value of production that results for a unit input change.

Renzetti and Dupont (2003) estimate the value of water using cross sectional industry data for the years 1981, 1986, and 1991 (this was based on Standard Industrial Classifications, which differ from UK Standard Industrial Classifications). The results are given in Table 2. Inflation factors and exchange rates are applied to transfer the values to 2004 UK pounds.

Table 2
Industrial value of water use £/m³

Manufacturing industry	1991 values (\$Can)	2004 values (\$Can)	2004 values (£UK)
Refined petroleum and coal products	0.288	0.362	0.157
Primary metal	0.107	0.134	0.058
Chemical and chemical products	0.072	0.090	0.039
Fabricated metal products	0.048	0.060	0.026
Beverage	0.038	0.048	0.021
Plastic products	0.032	0.040	0.017
Paper and allied products	0.031	0.039	0.017
Transport equipment	0.025	0.031	0.014
Non-metallic mineral products	0.023	0.029	0.013
Wood	0.020	0.025	0.011
Food	0.017	0.021	0.009
Rubber product	0.006	0.008	0.003
Textile products	0.005	0.006	0.003

Notes: inflation calculator: <<http://www.bankofcanada.ca/en/inflation-calculator.html>>.

Prevailing £–\$Can exchange rate: <<http://www.x-rates.com/calculator.html>>.

In transferring these values to Scotland and Northern Ireland, we make some strong assumptions. Perhaps the most basic assumption is that industrial water use is similar between the industries of the two countries. As OECD member states with similar GDP levels this is not an unreasonable assumption. Industrial processes are likely to be similar between internationally competitive producers. However, in applying inflation to the figures for 1991, there is an implicit assumption that there has been no change in water use in industrial processes (i.e. there have been no efficiency improvements since 1991). This is a strong assumption that is unlikely to hold in practice. For this reason in particular, the values above are only indicative of the relative value of water use between industrial sectors.

5.6. Hydropower generation in Scotland

A productivity approach to the value of water in power generation is difficult to use because of the highly distorted nature of market prices for energy, and especially due to UK government commitments to support renewable energy production through the Renewables Obligation. The latter essentially binds industry to source a percentage of energy from renewable sources. An alternative means of valuation is to compare the costs of generating electricity with hydropower and the costs of alternative generation technologies. The relevance of the value per kilowatt hour (kWh) produced using alternative technologies depends on the current situation insofar as it is important to define what the most likely alternative to satisfy short term and long term supply.

Gibbons (1986) describes three methods of calculating the economic value of water used in hydropower based on the different scenarios under which a given country might use hydropower production. These are summarised in Table 3 (adapted from Gibbons, 1986).

The choice of value depends on the alternative to generation with hydropower. The Scottish Executive (Scottish Executive, 2001) has suggested it may be necessary to modify the operation of hydropower facilities where negative impacts need to be mitigated. Therefore, a short run marginal value might be most appropriate where there could be temporary restrictions on water management and short-term displacement to other types of generation. On the other hand, a long run average value may be more appropriate in consideration of potential new hydropower developments.

The short run marginal value of water for hydropower generation is assessed in a paper by Macleod et al. (2006). This paper estimates the volume of water flowing through hydropower turbines based on power output, efficiency, and the working head of the scheme (the distance that the water falls through the turbines). The costs associated with hydropower generation are estimated and compared to the costs of generation using other technologies (using figures from the Royal Academy of Engineering, 2004). In conjunction with figures for overall generation, this allows

Table 3
Potential methods for valuing water use for hydropower

Method	Assumptions	Measurement of value	Interpretation for Scottish hydropower
Short run marginal value	All capital investment is fixed, and reduced water availability for hydropower generation displaces generation to an alternative source. Therefore, a temporary increase in alternative generation occurs, without requiring capacity increase.	Alternative source production less hydropower production costs (per kWh), not including capital outlay, depreciation or other longer-run costs.	Suited to measuring value in a context where abstraction for hydropower may be limited based on river flow rates, in order to preserve habitats or ecological health.
Long run replacement capacity value	Water availability restrictions create a need for augmentation of alternative capacity, hence the 'replacement' value.	The cost (per kWh) of new non-hydro capacity, less the foregone hydropower production costs.	Most suited to a situation where overall reductions in hydropower capacity are expected, for environmental or economic reasons, e.g. habitat replenishment, or avoidance of opportunity costs.
Long run average value	This represents the long-run value of water relative to alternative sources. It reflects the efficiency of hydropower generation's dependence on water itself and available feet of head.	Difference between total costs of the non-hydropower generation, less the total costs of hydropower generation.	Relevant to long term consideration of the value of water in hydropower, relative to long term alternatives for power generation. Most relevant to situations where hydropower capacity expansion is environmentally feasible.

Table 4
Short run marginal value of hydropower

	Cost of electricity (p/kWh)	Total value of water to hydro (£)	Average value of water to hydro (p/m ³)
Coal fired PF plant (no CO ₂ charges)	2.5	9,907,806	0.049
Coal fired PF plant (CO ₂ charges of £10/tonne)	3.3	36,402,527	0.180
Gas CCGT (no CO ₂ charges)	2.2	–27,715	0.000
Gas CCGT (CO ₂ charges of £10/tonne)	2.6	13,219,646	0.065
Nuclear fission plant	2.3	3,219,646	0.016
Onshore wind (no standby)	3.7	49,649,888	0.245
Onshore wind (with standby)	5.4	105,951,171	0.523
Offshore wind (no standby)	5.5	109,263,011	0.539
Offshore wind (with standby)	7.2	165,564,294	0.817

for calculation of the average value across all schemes in Scotland. The results are presented in Table 4 (MacLeod et al., 2006).

The most probable short-term alternative to hydropower would be coal or gas fired generation, or nuclear energy. The value of water for hydropower is higher when compared to onshore and offshore wind power, since these latter technologies are associated with greater capital costs. Although these costs are predicted to fall over the next 15–20 years (Policy and Innovation Unit (PIU), 2002), they are likely to remain high in comparison to other technologies. The value may also change if charges associated with emissions of carbon dioxide increase. Based on a hypothetical charge of £10/ton of CO₂, the value of water for hydropower increases from 0.049 to 0.180 p/m³ when compared to coal generation and from 0.000 to 0.065 p/m³ when compared to CCGT (gas).

It is important to note again at this point that this report does not consider the environmental costs or benefits associated with hydropower, since it concentrates on the benefits to water users only. However, there has been

significant debate about the potential positive and negative impacts of hydropower on the aquatic environment and in meeting renewable energy generation targets.

6. Summary and conclusion

Table 5 summarises the values derived in this study. There is clearly a significant disparity in value across sectors, for example the divergence between agriculture and hydropower is noteworthy. It is important to note however that the estimates are not all directly comparable. Abstracting from the different units of value (e.g. volumetric versus non-volumetric basis), the estimates are also an artefact of the decision on what uses to actually value. The decision on socially valuable uses can be determined by casual observation, but, the choice then dictates the different valuation methods used, which in turn generate different estimates of value.

Relating back to the WFD, implementation agenda these values do illuminate the potential for conflict if resource costs include the definition of opportunity costs

Table 5
Summary of the valuation techniques and results for sectors considered

Sector	Valuation technique	Key assumptions and limitations	Marginal/ average/total value	Value
Households	Gibbons' willingness to pay formula	Assumes all consumers pay volumetric charges levied to metered customers in England, Wales and Scotland Includes value of both clean and dirty water	M	0.102–0.244 p/m ³
	Benefits transfer from stated preference study	Only considers value of supply of clean water	M	0.067 p/m ³
Agricultural irrigation	Net-back analysis	Assumes that the West Pfeffer catchment is representative of other areas where potatoes are irrigated Value includes both naturally available water and water applied through irrigation	T	£5128/ha
	Transfer of net-back analysis	Data from England and Scotland combined despite different agricultural support arrangements and climate	A	23–138 p/m ³
Aquaculture	Avoided cost	Costs calculated based on running costs of the largest effluent filters bought without a loan Considers water use for disposal of solid waste only Assumes filters remove all solid waste	A	0.126 p/m ³
Salmon angling	Benefits transfer of travel cost method study	Assumes salmon anglers in Donegal are representative of others throughout Scotland and Northern Ireland	T	£175/day
Industry	Benefits transfer from marginal productivity approach study	Industrial water use in Scotland and Northern Ireland assumed to be the same as for Canada	M	0.3–15.7 p/m ³
		Assumes no improvements in water efficiency since 1991		
Power generation	Avoided cost	Compares generation costs associated with hydropower with generation costs from other fuels and technologies	M	0.00–0.049 p/m ³ (Compared to gas, nuclear and coal) 0.245–0.817 p/m ³ (Compared to windpower)

Note that average and marginal values are not strictly comparable.

outlined earlier. The implication may be that in the context of localised scarcity, water can possibly be better allocated to increase overall welfare. For example, where hydro-power impoundment precludes flow and recreational use for anglers downstream. In such cases one has to question the role of opportunity costs and whether the WFD has the radical intent of promoting resource transfers or whether it merely means to operate within the status quo of water rights. Whatever the intent of the WFD we should be cautious in being judgmental about which uses are more socially valuable and which impose costs on wider society. In the first place even if historically allocated resource claims can be contested, specific users do argue their allocation on the basis of vital industries. Water use does not only provide private economic benefits, but can also have important social and environmental impacts, both directly through water use and through the impacts of the sectors using the water. There is thus no prior assumption that reallocating water resources leads to higher welfare outcomes. Moreover, even if the intent of the WFD is to consider the full resource (i.e. including opportunity) cost the practical question of resource trading has to be adopted in practice. Currently the institutional arrangements do not exist to make this practical. In technical terms water trading is simply not always feasible. The early logic of the

WFD and associated guidance were fairly clear in terms of what they implied about cost recovery. But subsequent guidance has been watered down somewhat as implementing agencies have come to realise the practical implications of following a strict economic interpretation. There is currently no one way of meeting the reporting criteria, and how states meet the ultimate objective of good status (including determining time extensions and less stringent objectives) is largely devolved. Some countries are sure to follow a more rigorous interpretation and the end of the process will bring some fairly interesting reading for those interested in water economics.

Acknowledgement

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Appendix A

Table A1 summarises the broad categories of valuation method.

Table A1
Methods for calculating the value of water use

Method	Comment
Direct estimates of the demand curve	Where there is information on water quantities demanded at different prices it is possible to calculate a demand curve, from which marginal willingness to pay can be estimated (Bachrach and Vaughan, 1994). This has been carried out for household demand, for which there is relatively comprehensive information, but as yet has not been undertaken for industrial demand.
Estimates of the impacts of water use on profits/production	Two main methods can be used to estimate the impacts of water use on profits and production: netback analysis and the marginal productivity approach. Netback analysis can be used for any sector where there is information on the costs of inputs to production and the value of the output. The analysis is based on the idea that the maximum that a water user would be willing to pay for water would be the difference between the revenue from production and the costs, i.e. total profit. Therefore, estimates produced using net-back analysis can be regarded as the upper bound of the WTP range for the particular activity. The marginal productivity approach is more complex. This uses detailed financial information on the costs of inputs to a process, including water, and the value of the output to form the basis of an econometric relationship. This model indicates how each of the inputs contributes to the value of the output. Using the coefficient on the relationship between water use and output (i.e. the change in output that would occur if input of water changed by one unit) provides an estimate of the value of water to that production process.
Estimates of the costs avoided by water use	Without actually studying demand relationships, the concept of alternative cost can also be used to value water. Using water may often be one of a range of possible production choices, but is chosen as the most convenient or least expensive. In this case, the use of water allows the organisation to avoid the costs of installing a more expensive technology. The cost of the least expensive alternative to water serves can therefore be used as a proxy for the maximum amount the user might be willing to pay for water. Depending on the manner in which this theoretical framework is implemented, the resulting water values can be average or marginal. This method can be used for water-cooling and hydropower generation.
Estimates based on revealed preference	Revealed preference techniques are often used to value environmental amenities based on the costs of associated goods or activities. The travel cost method is used to assess the value of recreational or amenity use of a water body. It is based on the idea that the value of water use is equivalent to the costs that the user faces in travelling to the water, including the cost of time taken to get to the water body and transport costs. Alternatively the hedonic pricing may be used to estimate the landscape value of a water body. Hedonic pricing compares the cost of property local to a water body with properties not benefiting from such a location in order to estimate the marginal value of proximity.
Estimates based on stated preference	In contrast to the methods mentioned above, stated preference methods attempt to place values on uses that cannot be related to direct market transactions. In this case it is normal to use a hypothetical market (contingent valuation) survey to ask people directly what value the change in water use or quality might have to them. These techniques require careful planning and can be time-consuming, but are versatile and the information can be useful to help uncover recreational use values and landscape values that are otherwise hard to estimate.

Appendix B. Estimated net-back value for water used for irrigation using data from the West Pepper catchment

Irrigation of potato crops serves mainly to increase revenues by increasing crop yield (t/ha) and quality (£/ha). Scabbed potatoes are not saleable as a high quality product, such as the packaged potatoes found in supermarkets, but are graded out to fetch a lower price in a market such as processing for chips or crisps. Average willingness to pay for water per hectare of crop as calculated in the equations below represents the private net benefit plus any volumetric or flat rate water charge that is levied against water abstractions.

Figures for yield (ton/ha), water applied to irrigated land (mm), total area irrigated, and revenue (£/t) were given in the SEERAD study of irrigation in the West Pepper catchment (SEERAD, 2002).

The margin per tonne produced over non-irrigation costs is calculated from crop market price and yield, less costs per hectare. SEERAD (2002) states that “[variable, non-water] costs were calculated as the sum of costs relating to the area grown (at £1253 per ha) and costs relating to yield

(at £31 per tonne)”. Fixed costs associated with production (e.g. capital costs for equipment) are not included in the calculations, since it is more appropriate to use only variable costs to represent marginal costs associated with production.

Non-irrigation costs (£/ha)

$$= 1253 (\text{£/ha}) + (31 \times \text{yield (t/ha)}),$$

Margin over non-irrigation costs (£/ha)

$$= \text{revenue (£/ha)} - \text{non-irrigation costs (£/ha)}.$$

The water applied is given in SEERAD (2002) in mm. This is converted into m^3 per ha by multiplying the irrigation figure in mm by 10 ($1 \text{ ha} = 10,000 \text{ m}^2$, $1 \text{ mm over } 10,000 \text{ m}^2 = 10 \text{ m}^3$).

Irrigation costs are calculated in SEERAD (2002) based on annualised depreciated capital costs plus variable costs of supplying irrigation demand. The cost of irrigation depends on how the farmer distributes his extraction between potential sources (river, reservoir, borehole, etc.), unless the extent of irrigation demand is such that all

capacity is required. SEERAD (2002) converted capital costs of its surveyed farms into annual costs by annuitising over the lifespan of hoses/reeels (the most common form of irrigation system in the UK), pipes and reservoirs over their respective lifespans, with 9% interest. The cost estimates also account for the effect of natural moisture levels on demand, in that variable costs for delivering the water via an irrigation system vary year to year. SEERAD (2002) used weather data for the period 1989–1998 in combination with a potato growth and quality model to

are received. Although this is the case for Scotland and Northern Ireland, care should be taken when applying these figures to other regions.

$$\text{Net-back value (£/t)} = \frac{\text{net-back value (£/ha)}}{\text{yield (t/ha)}}$$

$$\text{Net-back value (£/m}^3\text{)} = \frac{\text{net-back value (£/ha)}}{\text{water use (m}^3\text{/ha)}}$$

Calculations based on yields and prices for the West Pepper catchment

	Yield (t/ha)	Non- irrigation costs (£/ha)	Revenue (£/ha)	Margin over non- irrigation costs (£/ha)	Irrigation requirement (mm)	Water applied to irrigated land (mm)	Water applied to irrigated land (m ³ /ha)	Irrigation cost (£/ha)	Margin over costs (£/ha)	Net-back value (£/ha)	Net-back value (£/t)	Net-back value (£/m ³)
1989	63.6	3215	10167	6952	170	112	1120	449	6503	6503	102.7	5.81
1990	70.8	3448	9181	5733	115	90	900	427	5306	5306	74.9	5.90
1991	61	3144	5616	2472	65	65	650	402	2070	2070	33.9	3.18
1992	67.3	3339	8127	4788	135	135	1350	472	4316	4316	64.1	3.20
1993	64.1	3240	8313	5073	105	105	1050	442	4631	4631	72.2	4.41
1994	61.2	3150	10909	7759	170	157	1570	494	7265	7265	118.7	4.63
1995	63.4	3218	11757	8539	155	130	1300	467	8072	8072	127.3	6.21
1996	69.3	3401	12839	9438	170	160	1600	497	8941	8941	129.0	5.59
1997	62.4	3187	5758	2571	55	55	550	392	2179	2179	34.9	3.96
1998	58.3	3060	5392	2332	40	25	250	331	2001	2001	34.3	8.00
Mean	64.11	3240	8806	5566	118.00	103.40	1034	437.30	5128	5128	80.0	4.96

Calculations based on yields and prices across Scotland

	Yield (t/ha)	Average market price (£/t)	Revenue (£/ha)	Non- irrigation costs (£/ha)	Margin over non- irrigation costs (£/ha)	Irrigation costs (£/ha)	Margin over all costs (£/ha)	Net-back value (£/ha)	Net-back value (£/t)
1997/98	44	76.29	3357	2617	739.76	437.3	302.46	302.46	6.87
1998/99	45	147.16	6622	2648	3974.2	437.3	3536.9	3536.9	78.60
1999/00	42	67.35	2829	2555	273.7	437.3	-163.6	-163.6	-3.90
2000/01	45	119.94	5397	2648	2749.3	437.3	2312	2312	51.38
2001/02	49	88.55	4339	2772	1566.95	437.3	1129.65	1129.65	23.05
Mean	45	99.858	4493.6	2648	1845.61	437.3	1408.31	1408.31	31.30

Figures of yield and price are from the British Potato Council. Note that the prices are not in 2003 equivalent.

run scenarios for each year calculating (based on prices defined by likely effects of dry or wet years on crop quality and quantity) likely yield and revenue.

As discussed in Section 9.3 above, the value of irrigation water is calculated as the margin of revenue over costs.

Net-back value (£/ha)

$$= \text{margin over non-irrigation costs (£/ha)} \\ - \text{irrigation costs (£/ha)}.$$

However, it should be noted that this figures assumes that there is no abstraction charge and no direct subsidies

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Long term changes in the eutrophication process in a shallow Mediterranean lake ecosystem of W. Greece: Response after the reduction of external load

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Abstract

Lake Pamvotis is a shallow Mediterranean lake located in Western Greece near the city of Ioannina. The lake has been recognized as an internationally important conservation site under European Community legislation due to its rich biodiversity. However, during the last three decades the trophic status of the lake has changed as a result of anthropogenic activity (among others irrigation and domestic sewage discharge), resulting in serious problems. Here we present data about the long-term development in eutrophication of Lake Pamvotis. Water samples were collected and analyzed (water temperature, pH, dissolved oxygen, nutrients, chlorophyll-*a*) during three monitoring periods: 1985–1989, 1998–1999, 2004–2005. The high nutrient concentrations in the lake water during the three monitoring periods, as well as its eutrophic to hypertrophic status reflect the degree of impact anthropogenic activity has had on the lake. Commencement of a restoration plan in 1995–1996, involving sewage diversion, led to a reduction in external nutrient load and consequently to lower in-lake nutrients and Chlorophyll-*a* concentrations. Orthophosphate concentration decreased by about 87%, nitrates fell below 1.20 mg/l, whilst the total reduction of inorganic N compounds showed a weaker downward trend, fluctuating between 0.39 and 1.24 mg N/l with an average value of 0.76 mg N/l. However, after a short-term recovery the eutrophic status of the lake remains eight years later (2004–2005), suggesting the importance of the internal loading process and the absence of the top-down effect of fish. This study provides evidence for the need of greater restoration efforts utilized in Mediterranean shallow lakes.

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Keywords: Shallow lakes; Eutrophication; Nutrients; Chlorophyll-*a*; External load

1. Introduction

The state and evolution of freshwater ecosystems are affected by a variety of biotic and abiotic factors, as well as by natural and human-induced processes that may differ both in duration and intensity. Lake ecosystems tend to maintain a state of equilibrium but their chemical resilience depends on certain site-specific factors and processes (Carpenter et al., 1999). In contrast to deep lakes, many shallow lakes can switch quite abruptly between different stable states, representing alternative equilibria; a hypothesis developed and established over the past 20 years and

summarized in Scheffer (1998). Lake eutrophication has been a major problem for decades. It involves a change in lake status from a macrophyte-dominated clear water state to a phytoplankton-dominated turbid state, with detrimental effects to the ecosystem (Portielje and Van der Molen, 1999). This “alternative states” model has been intensively investigated, whilst the need for clearer definitions in order to describe these situations has been addressed by Rojo and Alvarez-Cobelas (2003), Naselli-Flores et al. (2003).

Studies on shallow lakes from north temperate climate clearly demonstrate that they alternate between clear and turbid water states in response to some control factors. There is evidence that nutrient control may be of greater priority in eutrophicated warm shallow lakes than in

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similar lakes at higher latitudes. The influence of nutrients appears to increase southward from the north temperate regions (Nöges et al., 2003), and this was probably manifested through naturally greater annual macrophyte abundance in warmer locations as a consequence of longer plant-growing seasons (Moss et al., 2004). The eutrophication processes, as a response to nutrient loading, consist of the “tools” in understanding the ecosystem processes. In response to a period of globally intensive eutrophication, an increasing interest in freshwater restoration has taken place over the last two or three decades (Villena and Romo, 2003). According to the previously mentioned biostability model, the first step in the recovery of shallow lakes is considered to be the reduction of nutrient loading and specifically the reduction in the concentrations of ortho-phosphate (Scheffer et al., 1993). Previous studies concerning mostly north temperate lakes have recorded a decline in phytoplankton biomass after a reduction in phosphates (Jeppesen et al., 2000; 1998a), although this relationship is not as clear in shallow Mediterranean lakes (Villena and Romo, 2003). Recently, Gonzalez-Sagrario et al. (2005) argued that the focus should be widened to incorporate the control of both nitrogen (N) and phosphorus (P) in the restoration of eutrophic shallow lakes.

Here we present the changes in eutrophication parameters (nutrients and phytoplankton chlorophyll-*a*) for the shallow Mediterranean Lake Pamvotis, during three monitoring periods, over the last 20 years. The main questions addressed are:

- (1) Are there any inter-annually changes in nutrient concentrations and chlorophyll-*a* as a part of a long-term development?
- (2) What is the long-term development of eutrophication after a reduction in phosphorus, associated with sewage diversion?
- (3) What are the most effective restoration measures for the recovery and conservation of lake ecosystems?

2. Materials and methods

2.1. Study area

Lake Pamvotis, NW Greece (39° 40'N, 20° 53'E) is a shallow Mediterranean lake with a mean depth of 4.3 m and a maximum depth of 7.5 m. The lake occupies an area of 22.8 km² (Table 1, Fig. 1) and is situated approximately 470.25 m above the sea level. The lake is located next to the city of Ioannina (150,000 inhabitants) and 40% of the catchment is used for agriculture. It is an ancient lake ecosystem, situated in a topographically diverse landscape on the western flank of the Pindus mountain range (Tzedakis et al., 2002), and in terms of biodiversity Lake Pamvotis is of global significance (Krystufek and Reed, 2004). The basin has no naturally occurring surface outflows and is recharged by karstic springs. Drainage

Table 1

Some morphometric, hydrological, physical, chemical features of Lake Pamvotis (after Romero et al., 2002; Kagalou et al., 2003a,b)

Volume (m ³)	9.1 × 10 ⁶
Surface (km ²)	22.8
Catchment area (km ²)	510
Max/mean depth (m)	7.5/4.3
Hydraulic retention time (y range)	0.84–0.9
Summer water temp. ± St.d. (Epilimn./Hypolimn., °C)	25 ± 0.5/20 ± 0.4
Conductivity (μS/cm)	393
pH (range)	6.70–8.94
Water budget (difference between winter–summer, m ³)	
Period 1985–1988 (mean)	–31900
Period 1998–1999	–26620
Period 2004–2005	–24200
Water level fluctuation range (winter–summer, m)	0.60–1.15

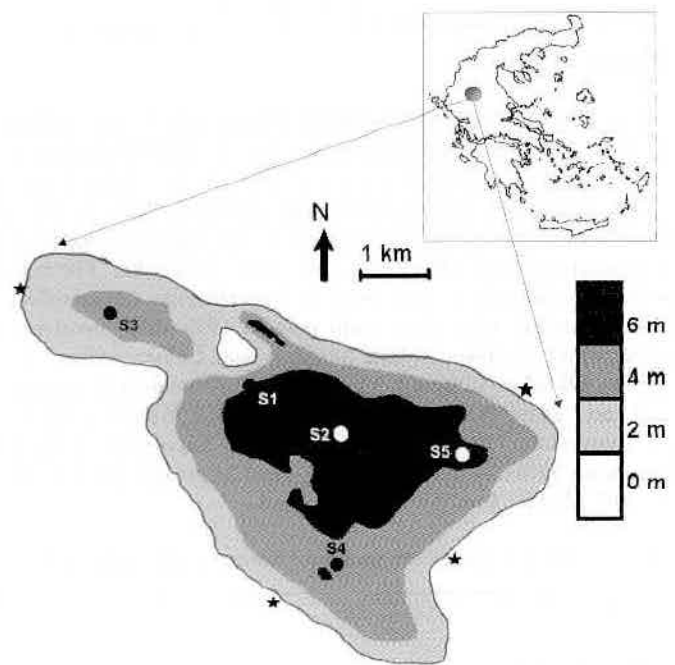


Fig. 1. Bathymetric map of the Lake Pamvotis (Greece). Dots show the sampling stations, asterisks show the inflows. Scale bar shows the different depths of the lake.

from the basin occurs through a system of sink holes that drain to the rivers Arachthos, Louros and Kalamas. The high topographic variability of this region provides a range of sheltered habitats. Indeed, a high-resolution pollen record from Lake Pamvotis reveals that temperate tree populations survived in this area throughout the last glacial period, owing to continued moisture availability and its varied topography, resulting in areas of relative ecological stability (Tzedakis et al., 2002). Lake Pamvotis is also a host to a number of endemic molluscan fauna (Frogley and Preece, 2004), thus enhancing the conservation value of the lake. Under the European Community Council Directive

on the conservation of natural habitats and of wild fauna and flora (Habitats Directive, EC, 92/43) Lake Pamvotis is listed in the Natura Special Conservation areas as “natural eutrophic lake with *Magnopotamion* or *Hydrocharition* type vegetation”. The characterization of the ecological status of lakes has become a legal imperative after the approval of the EC Water Framework Directive.

During the last three decades, anthropogenic activity (for example, irrigation and domestic sewage discharge) has altered the trophic status of Lake Pamvotis and caused serious problems (Stalikas et al., 1994; Kagalou et al., 2001; Kotti et al., 2000). In the 1995, sewage diversion to a treatment plant begun. During the 1970s, the submerged vegetation of Lake Pamvotis was dominated by nutrient tolerant species, with *Ceratophyllum demersum*, *Potamogeton perfoliatus*, *P. pectinatus*, and *Myriophyllum spicatum* being the most common. The floating-leaved species *Nymphaea alba*, *Nuphar lutea*, and *Nymphoides peltata* were evenly distributed and occurred in many areas of the lake (Ganiatsas, 1970). According to the testimonies of fisherman in the late 1980s, the whole bottom of the littoral zone of the lake was almost totally covered by submerged vegetation, dominated by *Myriophyllum spicatum* and *Potamogeton* species. Since 1986, the lake has been stocked with the exotic herbivorous species (*Ctenopharygodon idella*) and planktivorous species (*Hypophthalmichthys molitrix*, *Aristichthys nobilis*) in order to control the excessive vegetation and to support fishery. Common carp (*Cyprinus carpio*) has also been introduced annually. A decline in species diversity of the lake during the 1990s was found by Sarika-Xatzinikolaou (1994) and Kagalou et al. (2003a,b), the latter study reporting a decrease from 25 to 5 species of the submerged macrophytes, with low abundancies.

Land use trends around Lake Pamvotis have changed during the last 30 years. Such changes include an increase in urban areas by approximately 26% and a decrease in agricultural land but characterized as intensive productivity area. Agricultural pressures include the over abstraction of lake water for irrigation, which has a detrimental effect on the hydrological balance, the application of large amounts of fertilizers and agrochemicals in the fields causing a reduction in water quality, and problems associated with waste disposal and the expansion of cultivations, usually by fires in reed bed vegetation.

2.2. Methods

Limnological data collected during three different periods (1985–1988, 1998–1999, 2004–2005) were analyzed in order to evaluate the trophic state of the ecosystem during the last 20 years. Surface samples (in duplicate) were collected bi-weekly at five sampling stations using a HydroBios water sampler (21 capacity). Key eutrophication parameters were examined, including $\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NH}_4\text{-N}$, soluble reactive phosphorus (SRP) and

Chlorophyll-*a*. In situ, temperature, pH, and dissolved oxygen were recorded using a WTW meter. Chemical analysis followed standard methods (APHA, 1989). Nitrates were determined spectrophotometrically by reduction to nitrite and following the method of diazotation and condensation with salicylate (RSD = 10%). Ammonium content was measured spectrophotometrically by the Nessler method (RDS = 10%). Determination of orthophosphates was made by the molybdenum blue method (RDS = 2%). Chlorophyll-*a* was determined spectrophotometrically, after the extraction of pigments with ethanol (Jespersen and Christoffersen, 1987). As there were no statistical differences in limnological parameters between the sampling stations, the measured values from all five stations were combined. The water level of Lake Pamvotis was recorded weekly at a marked point close to the constructed outlet of the lake. Changes in the volume of the lake (Table 1) were calculated by multiplying lake level change by lake surface area.

2.3. Statistical analysis

Analysis of variance (ANOVA) (Zar, 1999) after logarithmic transformation of the measurements was used in order to compare the limnological parameters within the three sampling periods. In addition, Spearman's rank correlation was used to evaluate the relationships between the physico-chemical parameters in each period.

3. Results

Morphometric, hydrological, physical and chemical data, as well as the water budget for the three monitoring periods are presented in Table 1.

3.1. Changes in nutrient level

Monthly averages of nutrients during the three periods are shown in Fig. 2. In 1985–1988 the concentration of the dissolved inorganic nitrogen (DIN) compounds fluctuated between 1.43 and 2.07 mg/l. Higher values were observed during the winter months while lowest concentrations appeared during late spring and summer. The most important form of DIN was the nitrates, contributing at the DIN pool with a percentage of 89–94%, followed by ammonia and nitrites.

Annual SRP measurements during the same period showed no clear trend and ranged between 0.72 and 2.86 mg/l, with maximum values being recorded during warm periods. The DIN/SRP ratio ranged between 1.03 and 1.23 with an average value of 1.10, suggesting a nitrogen limitation.

After the diversion of sewage (1995–1996) the external nutrient load decreased significantly, resulting in lower in-lake nutrient concentrations, as seen in the measurements during 1998–1999 (Period 2) (Fig. 3). Statistically significant differences were observed in nitrates (ANOVA,

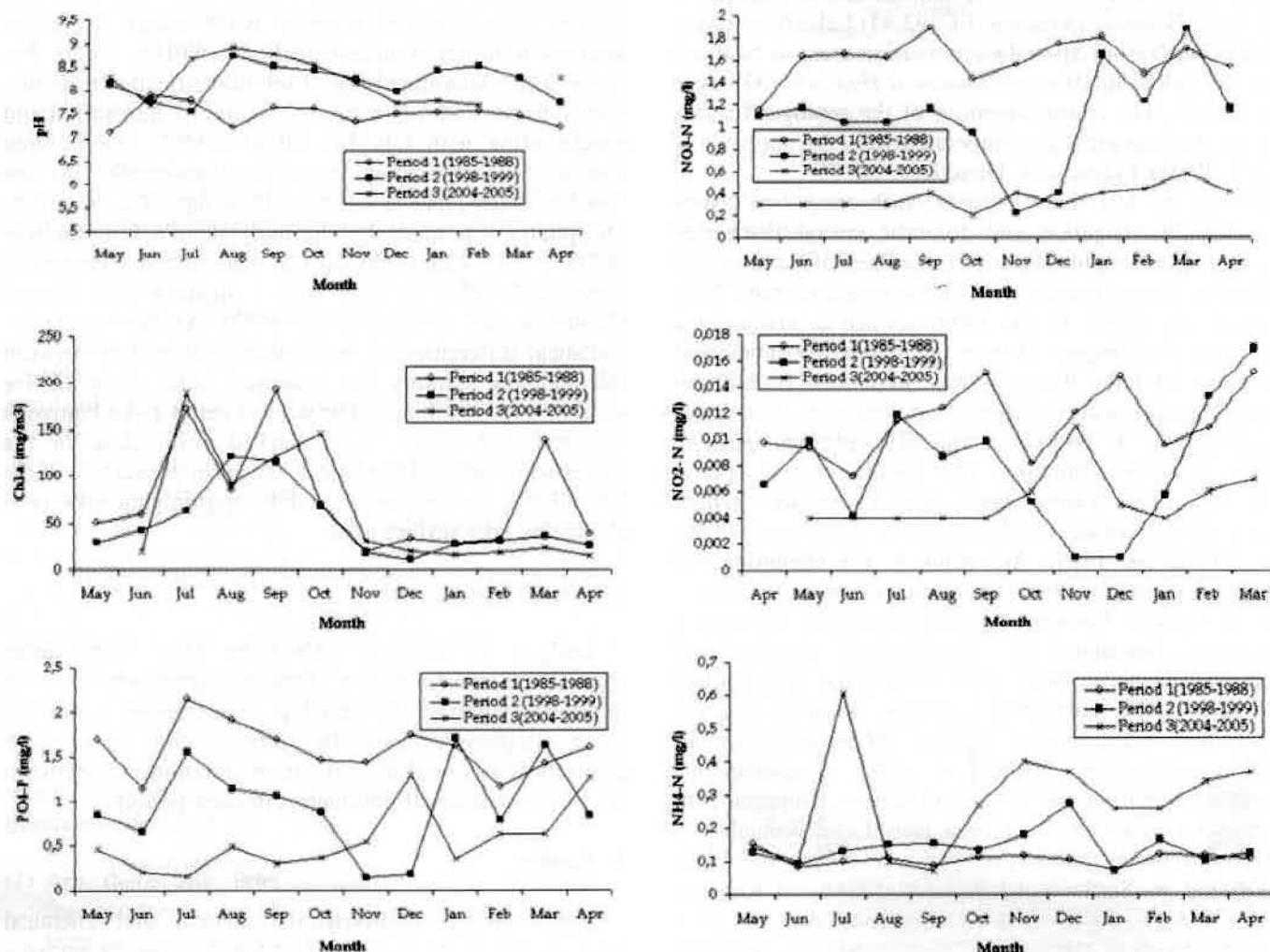


Fig. 2. Inter-annual variation of some physicochemical parameters (temperature, pH, dissolved oxygen, NO₃-N, NO₂-N, NH₄-N, PO₄-P, Chl-a) in the three monitoring periods.

$F = 149.97$; $P < 0.001$), nitrites ($F = 1.91$; $P < 0.1$) and phosphates ($F = 87.41$; $P < 0.001$) concentrations. Orthophosphate concentration decreased by about 87%, nitrates fell below 1.20 mg/l, whilst the total reduction of inorganic N compounds showed a weaker downward trend, fluctuating between 0.39 and 1.24 mg N/l, with an average value of 0.76 mg N/l. The annual pattern of nitrogen compounds showed similar trends as those measured in 1985–1988 (Period 1). The main DIN compound (nitrates) showed higher values during wetter months than during drier months and this may be attributed to nitrogen input from the catchment (Fig. 2). There is evidence of nitrate uptake towards the end of spring, resulting in low concentration during summer. With regard to ammonium, higher concentrations were apparent in late summer, during the warm period and during the months when the water level of the lake was high. SRP values were higher during the warm periods and during the months of high water levels (e.g. winter months). The

maximum drop in water level was 1.15 m (Table 1) and occurred between spring and the end of summer. The range in the DIN/SRP ratio changed from 1.61 to 17.52 during the second monitoring period and this was due to the comparatively smaller reduction in nitrogen, leading to an increased N/P ratio.

The measurements taken in 2004–2005 (Period 3), eight years after the sewage diversion, show that nitrates undergo a further decrease (Fig. 3), although the inter-annual pattern is quite stable with an accumulation tendency during the winter months. Ammonium concentration seems to increase during the summer months (Fig. 2). In winter the lake DIN was largely NO₃-N and in summer largely NH₄-N. In-lake orthophosphates concentrations appeared to increase significantly with an average value of 0.19 mg/l whilst the minimum concentration was recorded in May 2004 (0.08 mg/l). DIN/SRP decreased (average 2.12), and this is due to the increase in the concentration of phosphates.

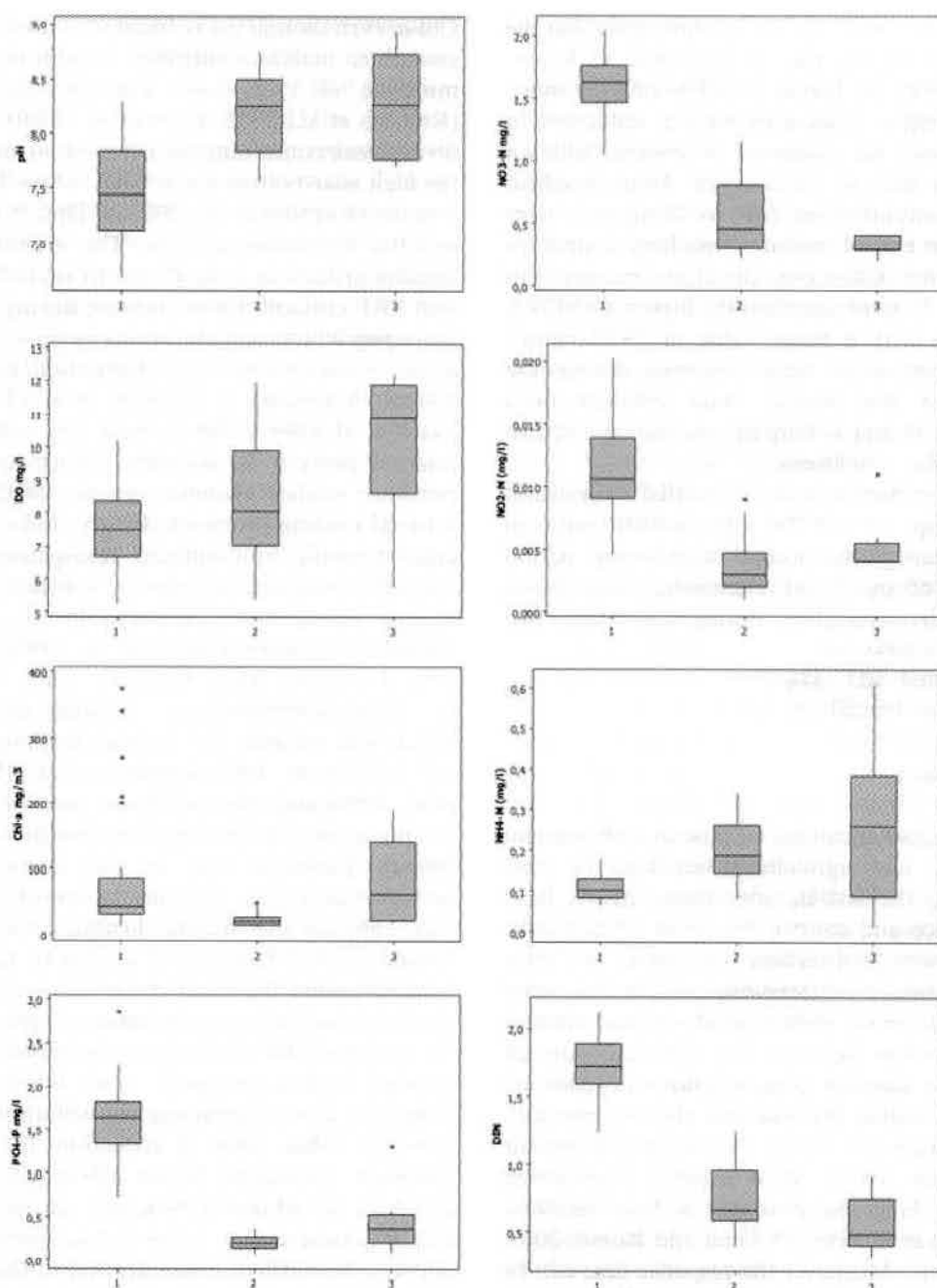


Fig. 3. Box plot of long term limnological features in Lake Pamvotis.

3.2. Temperature, pH and dissolved oxygen trends

The changes in the water temperature of Lake Pamvotis during the three monitoring periods followed the typical seasonal pattern of a Mediterranean shallow lake (Fig. 2). Summer epilimnetic values varied between 22 and 32 °C, whilst during winter the range was 4.2 to 8.0 °C. Statistically significant differences were observed among pH values between the first monitoring period (1985–1988) and the two other monitoring periods (1998–1999 and 2004–2005) (ANOVA $F = 21.54$; $P < 0.001$), indicating that there is a shift to more alkaline conditions. Typical annual

dissolved oxygen (DO) patterns were also encountered, with lower DO concentrations recorded towards the end of summer and higher values recorded during the winter months. No statistical differences were found between the periods studied.

3.3. Response of phytoplankton Chlorophyll-a to nutrient changes

Period 1 (1985–1988) Chl-a monthly averages are shown in the Fig. 2. The annual mean concentration was 76.91 mg/m³ and the highest values were recorded during

the warm periods. The values of Chl-*a* demonstrate that the trophic classification of the lake is eutrophic to hypertrophic (OECD, 1982). In Period 2 (1998–1999) a sharp decline in chlorophyll-*a*, associated with a reduction in nutrient input, follows the diversion of sewage, with an annual mean Chl-*a* level of 21.21 mg/m³ being reached. Increased Chl-*a* concentrations (up to 20 mg/m³) were recorded during the end of summer, reaching a peak of 45.9 mg/m³ in October. Chl-*a* concentrations measured in 2004–2005 (Period 3) were significantly higher (ANOVA $F = 2.51$; $P = 0.09$) with a mean value of 79.23 mg/m³. Even higher concentrations were observed during the warmer months of this period, with concentrations fluctuating between 91 and 189 mg/m³, indicating a return of strong hypertrophic conditions.

Spearman rank correlation analysis revealed a significant positive relationship ($R = 0.706$; $P = 0.010$) between Chl-*a* and SRP during the second monitoring period (1998–1999), whilst no significant relationships were found concerning the above variables during the other two periods.

4. Discussion

4.1. Phosphorus budget

Many lakes are highly eutrophic because of high nutrient loads from sewage and agricultural activities in their catchments. During the last decades many efforts have been made to reduce and control the input of nutrients, mostly P, through sewage diversion. According to Cullen and Forsberg (1988) there are three responses in lake water quality parameters after the reduction of external nutrient loads. The relationship between the external nutrient loading and in-lake nutrient concentrations depends on processes occurring within the lake and thus on physical, chemical and biological parameters and variables (Portielje and Van der Molen, 1999). Most external P-reduction studies in shallow lakes have shown a long recovery hysteresis (Jeppesen et al., 1991; Villena and Romo, 2003; Beklioglu et al., 1999). Moreover the response time can be highly variable in shallow lakes due to internal loading, the magnitude of the former external loading and the hydraulic retention time (Jeppesen et al., 1991; Sondergaard et al., 1993). However, there are also case studies demonstrating an almost immediate response after nutrient reduction (Chen et al., 2003).

Lake Pamvotis has a long eutrophication history (Anagnostidis and Economou, 1980; Albanis et al., 1986; Stalikas et al., 1994; Kagalou et al., 2001, 2003a,b) due to the heavy point and non-point loading of nutrients, with cyanophyte blooms occurring since 1978 (Anagnostidis and Economou, 1980). Reduction of external P-loading from 1.07 g P/m² y during the period 1985–1988 (Kousouris et al., 1989) to 0.75 g P/m² y after sewage diversion (Romero et al., 2002) resulted in a major decline in in-lake SRP concentrations, which was followed by a reduction of

Chl-*a*, even though the reduced concentration was still high enough to maintain eutrophic conditions. Sediment accumulation of P in Lake Pamvotis has been observed (Romero et al., 2002; Kotti et al., 2000) although there is no evidence concerning the net internal loading rate, except the high near-bottom water SRP values during the warmer months (Kagalou et al., 2003a). Thus it is not possible to test the hypothesis directly. The importance of internal loading process in Lake Pamvotis is confirmed by the fact that SRP concentrations increase during summer months, exceeding winter concentrations by up to 200–300% with a winter–summer water level fluctuation, ranging from 80 to 120 cm. According to Jeppesen et al. (1997) and Sondergaard et al. (1999), this increase can only be the result of internal process. In addition, information derived from previous studies (Romero et al., 2002) highlights the internal loading processes. Firstly, Lake Pamvotis experiences periodic wind-induced resuspension of its bottom sediments and lake currents are substantially important in driving resuspension (Romero et al., 2002) and thus phosphorus release (Ekholm et al., 1997; Jones and Welch, 1990; Fan et al., 2001). Secondly, many of the stocked fish are plankti-benthivorous, bottom dwelling cyprinids, which will enhance the internal loading process (Tartrai and Istvanovits, 1986; Jeppesen et al., 1990; Sondergaard et al., 1990) and affect predatory control. Furthermore the disappearance of submerged macrophytes (Kagalou et al., 2003a), probably due to the introduction of large herbivorous species, and thus the loss of habitat complexity may enhance the internal loading process (Graneli and Solander, 1988; Gonzalez et al., 1988). Thus, in terms of P concentrations, the arrest in the recovery of Lake Pamvotis observed during the last monitoring period (five years after the recorded SRP decline) may be explained by the intense internal loading processes, since internal loading is the dominant factor explaining the variation in P concentrations of lakes after a reduction in external loading (Diederik and van der Molen, 1994). According to Portielje and Van der Molen (1999), after an increase in the ratio $C_{\text{lake}}/C_{\text{in}}$ (where C_{lake} is the in-lake nutrient concentration and C_{in} the nutrient concentration of the incoming water) following a reduction of external load, a decrease in $C_{\text{lake}}/C_{\text{in}}$ may be expected again after some years when the P-content in the top sediment layer has moved towards equilibrium with the concentrations in the overlying water column. The time needed for this recovery can vary largely between lakes, and may in some cases take decades (Jeppesen et al., 1990). The present average SRP in-lake concentration is 0.19 mg/l for Lake Pamvotis, far from the recently suggested threshold of <0.05 mg/l needed to avoid algal turbid states in Mediterranean shallow lakes (Romo et al., 2004). The extremely high abundance of the planktivores (mainly silver carp, bighead carp and YOY common carp) (Kagalou et al., 2003a) also contribute to the increase in internal P loading. Many studies have demonstrated a significant internal P reduction after fish removal, followed by chlorophyll-*a* reduction (Jeppesen

et al., 1990, 1991). Concerning the role of planktivores on P dynamics, Romo et al. (2004) found a slight, significant, direct effect of planktivorous fish on SRP in-lake concentration when macrophytes covered the bottom. Moreover, the removal of carps substantially reduced total phosphorus availability in the water column in the Turkish lake Eymir (Beklioglu et al., 2003). Planktivory markedly influences zooplankton community, changing nutrient availability and also nutrients recycling rate (Fernández-Aláez et al., 2004). In addition plankti-benthivorous fish contribute to the re-loading of the water column with “new” nutrients from outside the nutrient cycle, also diminishing the P-accumulation rate in the sediment (Karjalainen et al., 1999). An intense annual fish restocking of Lake Pamvotis has occurred over the last decade in order to meet the requirements of local fishermen. Additionally, the absence of an adequate predator results in high phytoplankton biomass, through minimizing the top-down control effects (Sondergaard et al., 1993).

4.2. Dissolved inorganic nitrogen concentration

Many shallow eutrophic lakes studies have shown a rapid decrease in nitrogen after a reduction of external N loading. In-lake DIN concentrations can be affected by catchment characteristics, terrestrial N-retention, denitrification and direct atmospheric DIN deposition (Kopacek et al., 2005). After the diversion of sewage Lake Pamvotis responded to N-reduction with a slight decline in the concentration of DIN, which persisted until the final monitoring period. A higher reduction in DIN might have been expected, but a significant ammonium loading was observed in DIN pool during the last warm months of Period 3. This late increase in the concentration of ammonium may also have been a critical point in the enhancement of eutrophic conditions (Gonzalez-Sagrario et al., 2005; Landkildehus, 2005). During summer periods, low lake levels in Mediterranean shallow lakes, including Lake Pamvotis, lead to a higher plant biomass and a greater denitrification effect (Ozen et al., 2005) in the presence of nutrient loading and high temperature. Changes in temperature may explain the inter-annual variability observed in nitrate concentrations, and temperature changes may also contribute to the long-term nitrate concentration changes. Climate studies for this region and for the Mediterranean region as a whole have reported that Greece entered a warm period after 1997, in parallel with the abrupt climatic warming which occurred in the North Hemisphere since 1994 (Feidas et al., 2004). The increase of the annual average temperature in relation to biogeochemical processes might be a critical factor affecting in-lake nitrogen dynamics, in addition to the intense agricultural activities in the catchment. On the other hand, the intense carp stocking that took place during last period may also be enhancing dissolved nitrogen levels and needs to be corrected (Jeppesen et al., 1998b).

4.3. Stoichiometry

After the first N-limited period, DIN/SRP ratio became greater than 10:1 (Havens et al., 2003), suggesting a P-limitation, whilst a nitrogen limitation is briefly evident during summer and winter months. As revealed from measurements taken during 2004–2005 (Period 3), overall nutrient concentrations in the lake did not reach sufficiently low levels to directly limit phytoplankton growth. A decrease in DIN/SRP occurred because phosphorus created a surplus supply and nitrogen became relative scarce. A nitrogen limitation is apparent during the last monitoring period.

As a consequence, cyanobacteria are predicted to become the most widespread phytoplankton group (Smith, 1983). According to Havens et al. (2003) and Smith et al. (1995), DIN/SRP ratios of less than 10:1 or TN/TP below 29:1 by mass (Smith, 1983) are considered to indicate strong nitrogen-limiting conditions, which favor the growth and proliferation of N₂-fixing cyanobacteria. Cyanobacteria blooms also occur in Lake Pamvotis, affecting the aquatic life of the lake (Gkelis et al., 2005; Papadimitriou et al., 2005). The temporary decline of Chlorophyll-*a* values was insufficient to change the trophic category of Lake Pamvotis, which maintained its eutrophic status. The results presented here agree with the observations from several Mediterranean shallow lakes, where a long turbid phase (80–100 µg/l Chl-*a*) corresponds well with in-lake P concentrations >0.1 mg/l (Romo et al., 2004; Temponeras et al., 2000; Mitraki et al., 2003). The Lake Pamvotis system became more eutrophic after a return of higher SRP values, with an apparent hypertrophication tendency and frequent cyanobacterial blooms occurring during warm months (unpublished data). Downing et al. (2001) estimate that average summer TP concentrations above 70 µg/l in lakes will provide an 80% probability of phytoplankton dominated by cyanobacteria. In Lake Pamvotis the soluble part of phosphorus alone is higher than 70 µg/l. During the second monitoring period (1998–1999) phytoplankton biomass coincided with SRP concentration. After a long time of excessive P loads it is possible that the capacity of a lake to assimilate P will decrease (Havens and Schelske, 2001) and thus the accumulated P favors a P-surplus and a long nitrogen limitation. Further research is needed to improve our understanding of all possible parameters involved (for example, light climate, metabolic processes, species composition, coverage of macrophytes) especially for Mediterranean shallow lakes.

5. Conclusions

The research on Lake Pamvotis serves as a further example of the valuable insight provided by developing a two-tiered approach to lake classification and assessment. The lake can be considered as a shallow eutrophic Mediterranean lake located at a high altitude and influenced by changes in climate.

The long-term eutrophication of Lake Pamvotis confirms that eutrophic to hypertrophic conditions have existed at least since the 1980s. Lake restoration efforts were traditionally focused on reducing the external phosphorus loading, leading to a significant decrease of in-lake phosphorus, even though the in-lake concentration was still high enough to maintain eutrophic conditions. Internal P-loading is expected to enhance the eutrophication and to reduce the lake's response time to external reductions in P load by a decade or longer. Besides the further reduction in external P-loading, the removal of some P-rich sediments may allow a more effective response and recovery. This approach must be very carefully considered due to the shallowness of the lake and issues concerning sediment resuspension. Concerning the top-down control, the abundance of detritivorous and the absence of piscivorous species cannot contribute to the cascading effects of fish. The possible introduction of a piscivorous species might have unknown consequences for the endangered endemic species *Phoxinellus epiroticus* and *Barbus albanicus*.

It seems that a future significant decline in P and a substantial removal of carps could act as a 'reverse switch' for the recovery of Lake Pamvotis and the re-establishment of the submerged vegetation. Fish removal may lead in a consequence of changes in the nutrient levels, as it has happened in many other cases, and thus in the improving of the water clarity. Although the fact that each lake is unique and that the response may be different in this warm Mediterranean lake compared to a cold-temperate one the general re-oligotrophication response pattern might be, more or less, the same. The degree of influence of these restoration measures needs to be assessed and monitored as part of an effective management plan for the lake. Whether the present activities associated with Lake Pamvotis (e.g. fishery, irrigation, navigation, agriculture) will sustain or constrain a recovery process is open to discussion. Moreover, the effect of climate changes for this Mediterranean lake may be greater than the environmental impacts already considered; something which is difficult to predict. Because Lake Pamvotis now falls under EC Habitats Directive, there is a requirement to maintain and restore the lake to a "favorable conservation status". This status will be achieved when specific structure and functions necessary for its long-term maintenance exist and which are likely to continue into the future.

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Environmental education for small- and medium-sized enterprises: Methodology and e-learning experience in the Valencian region[☆]

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Abstract

The last decades have shown an increasing social demand for environmental awareness, which firms are inevitably required to adapt to. More and more, small- and medium-sized enterprises (SMEs) are finding it necessary to train their staff in environmental issues if they wish to survive in a market where it is no longer sufficient to excel in price competitiveness exclusively, but where quality, service and environmental standards also play an important role.

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1. Introduction

One of the most important goals to achieve sustainable regional development is, along with social and individual understanding, environmental sensitivity. The last decades, especially of late, have shown a change in the characteristic behaviour of advanced markets from markets which demand competitive prices to those which, in addition to price competitiveness, value other criteria such as quality, service and environmental awareness (Hale, 1996). It is not surprising therefore, that in response to the new market

demands, enterprises should eagerly seek to minimise their “subtracted value”, a concept introduced by Smith (1971) in location decisions. As a consequence of the growing social environmental concern on the one hand, and of the strategic interest of firms on the other, companies are now required to draw a sound environmental compromise with the location, the use of natural resources, the design, the production and management (Macris and Georgakellos, 2006). The degree to which this is carried out successfully will strongly depend on workers aptitude (Henning, 1981). The more qualified the human resources are in environmental issues, the stronger the commitment with the company’s natural surroundings and consequently, the greater the benefits incurred by the firm (Boyle, 1999). It is not surprising thus, that environmental training is considered “one of the most important tools to develop human resources and facilitate the transition to a more sustainable world” (Agenda 21, 1992, Chapter 36).

Given that these requirements are relatively new and that education centres have only recently began to offer environmental training—not without difficulties (Boyle, 1999)—there exists a gap between the level of environmental expertise of the human resources and the level required for the company profile. This lack of formation exists even within business school teaching staff and

[☆]This paper presents a methodology to aid in the decision-making process of potential environmental training programmes directed at small- and medium-sized enterprise (SME) workers. Three indexes that describe the potential programmes, namely the present demand index, the prospective demand index and the course quality index are analysed and integrated, giving way to a ranked course proposal from which to select the most appropriate offers. An application and subsequent evaluation of the methodology for the case of SMEs within the Valencian Region reveal a robust and reliable means to decide on the production of courses which not only respond to present and prospective demand, but are also of sufficient quality to satisfy the workers involved in this training program.

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consequently management is not adequately prepared to account for the environment as a key issue in decision-making processes (Barratt, 2006; Pretorius, 2004; Dominik et al., 2003; Bunch and Finlay, 1999). This is particularly problematic for small- and medium-sized enterprises (SMEs).

SMEs play an important role in the economic development of a nation. However, they are not exempt of environmental contamination. In fact, within the European Union, SMEs contribute significantly to the level of environmental pollution (Smith et al., 2000). What is more, a poor level of development in environmental strategies can be observed for this kind of company. One of the most influential factors for this behaviour is the scarcity of environmental training among their employees (Brío and Junquera, 2003); a problem aggravated by the lack of necessary resources and a reduced turnout in environmental training programmes as opposed to larger companies (Arora and Cason, 1995). Encouragingly though, case studies reveal that businesses show notable enthusiasm to promote environmental awareness among their human resources (Way et al., 2002; Commission for Environmental Cooperation, 1997).

If the necessity to educate SME employees in environmental issues is evident, so is the need to rigorously decide on environmental training programmes, with the purpose of optimising their resources and exploiting educational investment to the full (Vezzoli, 2003; Albores et al., 2000). In fact, *“for people currently working in industry (and institutes, government, authorities) and who still have 20 or 30 years in which they too are responsible for the environment, postacademic courses are still the only way to get the skills and knowledge required”* (Venselaar, 1995). These programmes should have a job-specific focus, aimed at filling the gaps in knowledge and skills that will help individuals find employment and be involved in environmental and development work (Agenda 21, 1992, Chapter 36). Furthermore, they should be based on local needs, expectations and conditions (Diduck, 1999).

To achieve this objective, the present study proposes a methodology to aid in the selection process of environmental e-learning courses directed at SME employees, via previous evaluation of the courses from a supply and demand point of view. Given the presence of multiple and conflicting criteria, this methodology proposes a group-decision multicriteria approach (Keeney and Raiffa, 1976) to assist in the process of decision making.

An application of this methodology is then presented for the case study entitled “Environmental e-learning programmes for the employees of SMEs in the Valencian Region (Spain)”, in which the authors have participated and which has been financed jointly by the European Social Fund and the Valencia University of Technology. The project involves an investment of over 4 million € for the development and execution of environmental e-learning courses directed at SMEs in the Valencian region. The scope of this learning project embraces a period of 6 years

beginning in 2002, of which the first year is dedicated to the design and production of e-learning materials and the last 4 years to the execution of the courses.

2. Proposed methodology

2.1. Objectives

For the case of SMEs seeking to undertake an environmental training agenda, the primary objectives of the study are defined as:

1. identification and definition of environmental training courses that most adequately meet the formation needs of SME employees;
2. the training programmes should not only answer to the current demand (present demand) for environmental training, the programme should also meet the demand in the medium run, which itself should at least include the 6 years period of the project;
3. the educational programmes should be of sufficient quality to satisfy the educational requirements of SME employees;
4. the methodology should incorporate a robust technique to assist managers in deciding upon the priority with which the training programmes should be executed, giving special focus to the optimisation of available economic and human resources (Hwang et al., 2004).

These objectives are formulated independently of the different education modalities, whether classroom learning, e-learning or mixed. Noting thus that the methodology proposed in this paper may be applicable to any of these cases, this study will focus on e-learning systems. Because of the costs inherent in electronic learning (for the most part the implementation of the web platform and the production of educational material), selecting the correct programmes is of critical importance (Desanctis et al., 2003). In fact, as suggested by Cloete (2001), ensuring success, effectiveness and quality of electronic learning systems, requires implementing a scientific approach that provides sound, systematic procedures and techniques to carefully plan and construct the system.

2.2. General outline

In the aim of accomplishing the objectives stated above, it becomes fundamental to determine a methodology that facilitates the selection process of environmental training programmes. As illustrated in Fig. 1, the method proposed merges an analysis of the demand for potential courses together with an analysis of the supply. A survey is conducted to define the present demand for environmental training and a statistical study of the results is carried out. Consequently, courses are classed in order of preference, thus complying with the first objective stated in the previous section and providing an answer to the question

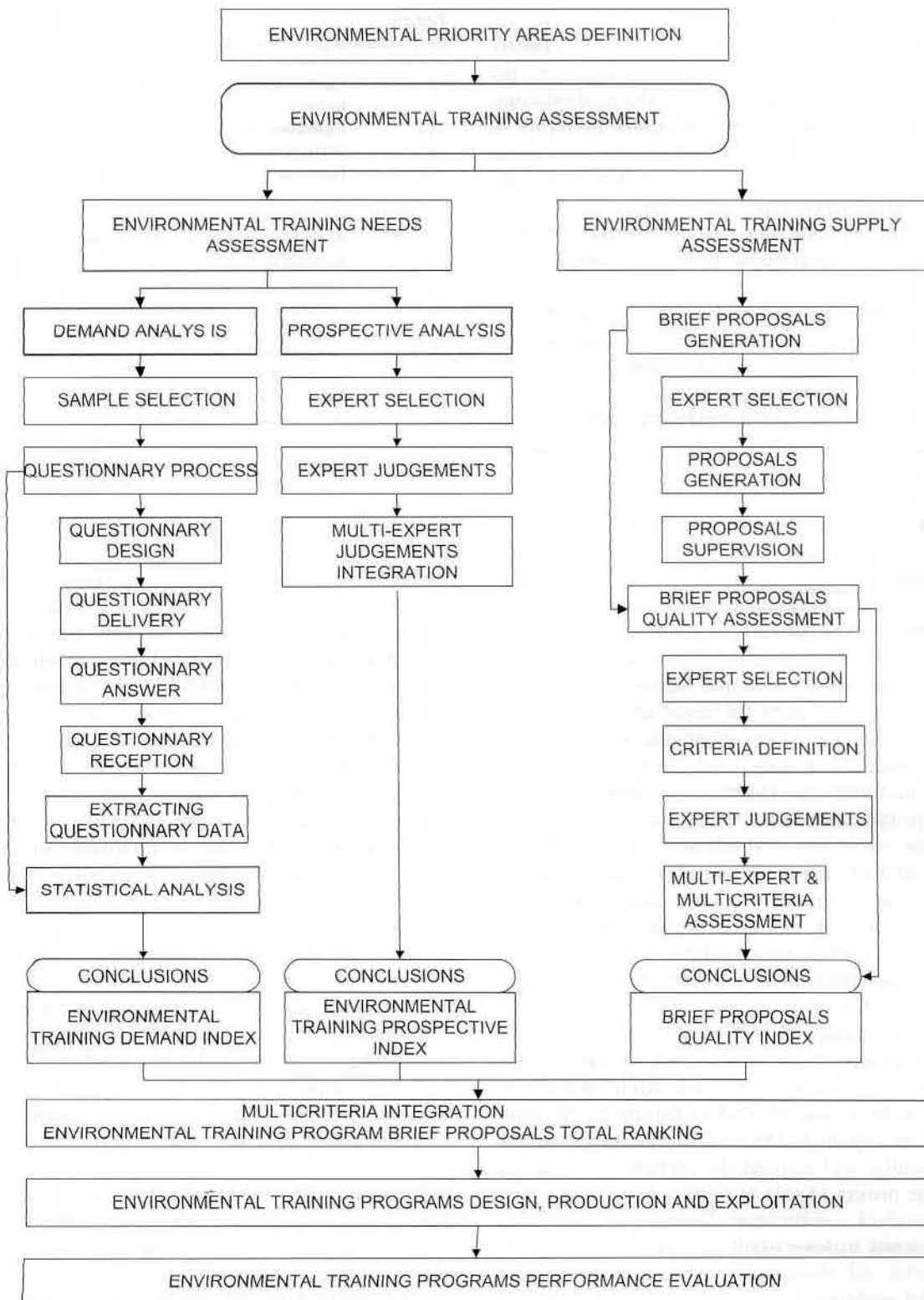


Fig. 1. Methodology layout

of whether there will be enough potential users to justify development costs. This is one of the most important and critical considerations prior to the development of an e-learning programme (Silver, 2004). Dealing with the second objective requires another set of rankings to be developed.

Multiple experts qualitatively assess the prospective demand thereby ensuring not only present demand, but also the future one. Accounting for future demand is of vital importance both for the organisation and for the individual learners involved. It provides a strategic means for SMEs

to sustain competitiveness in the long run and for individuals to devise long-term career goals (Ismail, 2002), and it also contributes to reduce the fixed cost per student of the initial investment. Next in the methodology, experts evaluate multiple course proposals in terms of quality to compute a third set of rankings and thus meet the third target. The three entries are then integrated following a multicriteria approach to generate the final overall ranking of potential environmental training courses. These techniques show particular adequacy for the solution of such problems, especially those within the environmental field (Kranjc and Glavič, 2005; Beccali et al., 2003). Having met the last target, it is left over to design, produce and execute the programmes. This task closely follows the methodology presented by Govindasamy (2002) in its advocacy for a pedagogic revision of the courses. Nevertheless, differences in execution tasks can be found.

3. Case study

3.1. Description

The purpose of the project entitled “Environmental e-learning programmes for the employees of SMEs in the Valencian Region (Spain)” is the production and execution of 24 educational programmes directed at SME workers and aimed at the development of the environmental competence of such companies to improve their individual capacity and performance. The basic requirements of the educational programmes are: (i) the content must be related to the environmental training required by the student's job and (ii) the maximum duration should not exceed 60 learning hours so as to make the course compatible with the job. To facilitate the application of the methodology, a set of topics related to environmental contents (hereafter referred to as environmental priority areas) was defined for the classification of the courses. For this purpose, proposals made by Diduck (1999) for environmental education in general and by Hale (1995) for environmental training in the industrial sector were considered. Finally, it was decided to use the classification proposed by the Spanish Ministry of the Environment, since it was similar and assisted the exchange of information within the project (Table 1).

3.2. Environmental training needs assessment

3.2.1. Demand analysis

According to the methodology proposed, the analysis of the demand was carried out prior to the conception of the first “outlines” of potential courses. The idea was to avoid a situation in which the results of the analysis are conditioned by the title of the course.

A survey of environmental training needs was carried out with a sample of 1415 individuals (workers), representatives of different business sectors and of firms of

Table 1
Environmental priority areas

1	Environmental management systems
2	Industrial processes. Best practices and mitigation measures
3	Environmental legislation
4	Sustainable rural development
5	Economics and the environment
6	Acoustics
7	Air pollution
8	Residual management and infrastructural maintenance
9	Renewable energies
10	Tourism and the environment
11	Remote sensing and geographic information systems
12	Landscape
13	International environmental lexicon
14	Environmental architecture
15	Environmental chemistry
16	Natural resource management
17	Technology and the environment
18	Natural disasters and emergencies
19	Environmental impact assessment

different sizes (from 1 to 250 workers according to the definition of SME) and who held a level of qualification which ranged from medium to high. For this survey, the total population accounted 193,063 individuals, and so for a confidence level of 95% in the worst case scenario ($p = q = 0.5$), the sampling error was of 2.6%, which lies well within the tolerance threshold required in the problem. The survey asked for general data on the academic qualification (level of studies), the position within the company and the size of the company. Specific questions were also asked regarding the familiarity and involvement with environmental issues. The questions were posed as follows:

- Have you had any previous education on environmental issues?
- Does your job share any relation to the environmental problem?
- In what areas would you need to enhance your environmental education?
- Would you be willing to complete a training course via the internet?

Similarly, official information was collected on the educational investment made by firms during the 5 years previous to the study and it was aggregated according to activity sectors. This information was considered necessary to evaluate the true commitment of the companies towards the education of their workers.

3.2.1.1. Qualitative results of the demand. Once the survey was processed, a Categorical Principal Components Analysis was carried out to reduce the dimensionality of the set of categorical data obtained. The results of the analysis are presented in Fig. 2. The interest expressed by the individuals on the environmental priority areas is

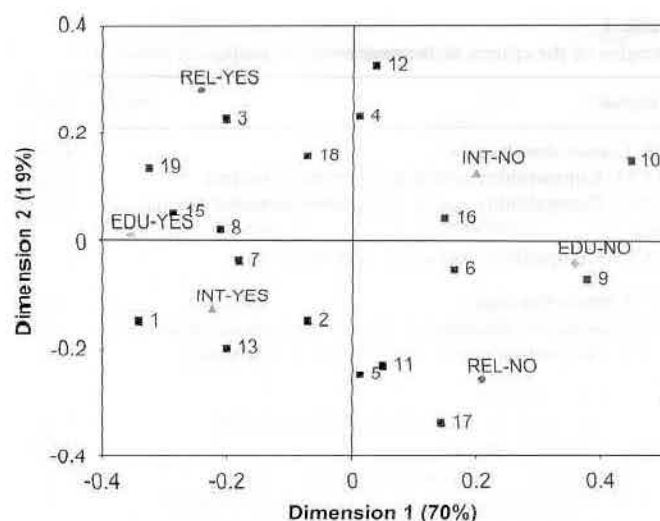


Fig. 2. Representation of the results of the categorical principal components analysis. INT "the individual is willing to undertake courses via internet", REL "the individual's job is related to environmental issues", EDU "the individual has previous education in environmental matters".

shown in the plane defined by dimensions 1 and 2 (89% of the explained variability). Those individuals whose current occupation is related to the environment are associated especially to the area of Environmental Legislation, while those with previous education in environmental issues are mainly related to areas 19, 15 and 8. In such cases, the educational material to be produced ought not to reiterate basic environmental concepts. Areas 1, 2, 7, 8, 13 and 15 are highly demanded by those individuals who are willing to undertake courses via the internet. On the other hand, areas 4, 6, 9, 10, 12 and 16 are requested by those who refuse on-line tuition. In the latter case, it is recommended that special care is taken when deciding upon the courses, as scarce predisposition of the students can negatively affect the performance of the course. Finally, area 14 is not represented in the graph because its scarce demand does not provide sufficient data to obtain a statistically significant result. What is more, because of the little interest expressed by the individuals surveyed, the development of e-learning courses in this area was not recommended.

3.2.1.2. Quantitative results of the demand. A quantitative analysis of the demand was performed on the basis of an indicator defined by the expression (Eq. (1)):

$$N_{epa}(a) = \sum_{j=1}^m V_j[a](0.3PT_j + 0.6RJ_j + 0.1)IR_j, \quad (1)$$

where $N_{epa}(a)$ is the index of the environmental priority area "a", $V_j[a]$ is vote of individual "j" on the environmental priority area "a" (yes = 1, no = 0), PT_j is previous environmental education of individual "j" (yes = 1, no = 0), RJ_j is relation of the job of individual "j" to

Table 2
Results of quantitative demand index

(i)	Environmental priority areas	$N_{epa}(i)$
17	Technology and the environment	52.73
9	Renewable energies	48.30
1	Environmental management systems	42.84
2	Industrial processes. Best practices and mitigation measures	42.13
5	Economics and the environment	37.60
16	Natural resource management	36.31
19	Environmental impact assessment	35.39
3	Environmental legislation	34.05
8	Residual management and infrastructural maintenance	33.98
7	Air pollution	31.13
6	Acoustics	29.28
11	Remote sensing and geographic information systems	27.82
4	Sustainable rural development	27.17
18	Natural disasters and emergencies	26.65
14	Environmental architecture	26.38
15	Environmental chemistry	24.44
10	Tourism and the environment	24.24
12	Landscape	21.44
13	International environmental lexicon	17.57

environmental issues (yes = 1, no = 0), IR_j is investment in employees training on the sector of economic activity to which individual "j" belongs.

This way, the importance of the opinion of each consulted individual was weighted according to their proximity to environmental issues in the respective industry. Given that the programme is oriented towards the necessities of SME workers, the most valued opinion is that expressed by an individual who has not only been trained, but whose job also actively involves environmental management.

The indicator is adimensional, and assumes values from the total number of votes emitted by the surveyed individuals (1415 answers). The selection of the priority areas was not exclusive hence each individual was allowed to choose as many areas as desired. To facilitate understanding of the order of magnitude to the decision makers, the data were normalised to percentage values (Table 2).

3.2.2. Supply analysis

3.2.2.1. Brief proposals generation. Following the methodology presented, the first phase of the supply analysis was the generation of proposals for educational programmes. It should be noted that these are not strictly courses; rather they provide an academic basis from which to develop the courses. Generating the proposals required making use of the conclusions derived previously from the study of the present demand. A total of 25 experts in environmental issues were selected from within teachers and researchers of Spanish universities and research centres, whose curricula demonstrated not only an expertise in those issues, but also pedagogic experience

Table 3
Brief proposals content

Item	
1	Name of the course
2	Environmental priority area
3	Key words
4	General objectives of the course
5	List of topics
6	Summary of the course
7	Duration
8	Level
9	Entry profile
10	Prerequisites
11	Leaving profile
12	Education modality (face-to-face, e-learning or mixed)

with SME workers. The issues in question were those related to the environmental priority areas with a highest index of demand. With the purpose of facilitating the management, the interpretation and the subsequent evaluation of the proposals, a standard document was devised (Table 3). A total of 150 proposals were generated by the experts and subsequently supervised by an academic supervisor, who had to examine and verify the coherence of the proposals as well as their relation to the particularly in-demand area (or areas) of environmental priority.

3.2.2.2. Brief proposals quantitative demand assessment. A demand index was developed for each brief proposal. For the case where a proposal is solely related to one unique environmental priority area, the value assigned is that of the latter, namely, $N_{epa}(a)$. If the proposal relates to multiple environmental priority areas, the value assigned is the mean

$$DI(i) = \frac{\sum_{k \in J(i)} N_{epa}(k)}{m}, \quad (2)$$

where $DI(i)$ is the demand index of proposal “ i ”, $J(i)$ is subset of environmental priority areas belonging to proposal “ i ”, $N_{epa}(k)$ is index of demand of environmental priority area “ k ”, related to proposal “ i ” and m is order of $J(i)$.

3.2.2.3. Brief proposals quality assessment. A second group of 15 specialists was selected to evaluate the quality of the 150 proposals generated. Their curricular profiles included knowledge of general and specific environmental topics, in addition to practical experience in the SME environment. It was required that the evaluating specialists had no relation (whether personal, geographic or institutional) with the experts who had generated the proposals. Following a multiexpert evaluation approach, every expert evaluated 30 proposals each. In this way, every proposal had undergone three different assessments.

Table 4
Weights of the criteria in the evaluation of quality

Criteria	Weight
<i>C1: Course identification</i>	0.091
C11: Compatibility course name–course contents	0.022
C12: Compatibility course name–environmental priority area	0.010
C13: Compatibility keywords–course contents	0.050
<i>C2: Course objectives</i>	0.239
C21: Adequate formulation of the objectives of the course	0.038
C22: Adaptation course objectives–course contents	0.201
<i>C3: Course contents</i>	0.471
C31: Adequacy course contents–course duration	0.045
C32: Content updating	0.120
C33: Adequacy of the sequence of the contents	0.078
C34: Adaptation course contents–education modality	0.067
C35: Adequacy course contents–course summary	0.029
C36: Adequacy course contents–course level	0.132
<i>C4: Student profile</i>	0.199
C41: Adequacy of the student’s entry profile	0.100
C42: Adequacy leaving profile–course contents	0.099

The evaluation process was carried out via the Delphi consulting method (Dalkey and Helmer, 1963), using a web platform developed throughout the project as recommended by Zhu and Dale (2001) on web-based decision analysis tools. The construction of this index took place via hierarchical modelling following the AHP method (Saaty, 1980):

- a hierarchy of evaluation criteria was established in two levels;
- the weights were determined by means of successive binary comparisons (eigenvector technique). Table 4 shows the results;
- a standard Likert scale (of 5 levels) was used for the evaluation of each “brief proposal”, which varied from total agreement to total disagreement as proposed by Bernstein (2005).

The entire process took place by the use of a multiexpert approach. In an initial sub-phase, the experts arrived at a consensus on the hierarchy of the criteria via group discussion. The experts’ opinions on the importance of the criteria were then introduced using the software Expert Choice 2000, and a qualitative scale appropriate of the AHP method was used (Saaty scale). The final binary comparison matrix was then constructed through the arithmetic mean of judgements, after which it was submitted to the experts for final assessment.

For the final calculation of the index, the criterion established for consensus was that the evaluations of each item should have a deviation smaller or equal to 1. If this was not the case, the evaluators were informed and the process was repeated in a subsequent iteration, as indicated

Table 5
Assessment results (excerpt of 20 brief proposals)

Index	Topic	QI	DI	PI	Rank		M(QI)		M(DI)		M(PI)	
					E	W	E	W	E	W	E	W
BP035	Electromagnetic pollution	91	100	100	1	1	0	1	0	0	0	1
BP026	Environmental management in metal-mechanic industries	93	80	100	2	3	0	1	0	1	0	0
BP059	Industrial waste management	100	100	75	3	2	0	1	0	0	0	1
BP025	Environmental management in textile industries	87	80	100	4	5	0	1	0	2	0	1
BP089	ISO-14000 norms and the implementation of environmental management systems	88	73	100	5	11	0	2	0	4	0	3
BP086	Integrated environmental management, quality and health and safety at work	83	81	100	6	7	0	1	0	2	0	1
BP136	Energy saving techniques in design and exploitation of industrial facilities	75	90	100	7	6	1	5	1	4	0	1
BP005	Storage of industrial waste	99	82	75	8	4	1	5	1	2	0	2
BP055	Fundamentals of environmental acoustics	89	72	100	9	12	2	3	2	4	0	3
BP138	Treatment of industrial liquid effluents	81	90	75	10	14	1	2	3	4	0	4
BP135	Electric energy saving techniques for the exploitation of industrial facilities	71	90	100	11	10	2	7	2	3	0	2
BP063	Management and analysis of data within the environmental field	78	81	100	12	13	3	3	2	2	0	3
BP028	Electromagnetic fields generated by electricity systems	64	100	100	13	8	3	10	3	6	1	1
BP134	Industrial ventilation systems and atmospheric pollutants treatment systems	78	80	100	14	15	2	4	2	3	1	2
BP099	Managing urban noise	99	62	100	15	9	3	6	4	9	3	2
BP144	Waste treatment with plasma	71	90	75	16	20	4	13	11	11	1	2
BP052	Wind power	64	92	75	17	29	5	12	6	14	4	3
BP022	Environmental audit and health and safety audit	89	77	75	18	18	4	4	4	1	1	1
BP133	Simulation of environmental processes	99	84	50	19	16	9	9	9	4	5	10
BP044	Design of solar systems of hot sanitary water	87	92	50	20	17	5	2	7	7	5	4

QI, quality index; DI, demand index; PI, prospective index; Rank, global ranking of the assessed proposal; M(QI), maximum position span due to QI weight variation; M(DI), maximum position span due to DI weight variation; M(PI), maximum position span due to PI weight variation; E, Electre III; W, Weighted Sum.

by the Delphi method. Once consensus was reached, the quality index (QI) of each proposal was developed from the following weighted sum:

$$QI_i = \sum_{j=1}^m \omega_j \mu_{ij} \Leftrightarrow \sigma_{ij} \leq 1, \quad (3)$$

where QI_i is the quality index of proposal “i”, ω_j is weight of criteria “j” (see Table 4), μ_{ij} is mean of the expert assessments of proposal “i” for criteria “j”, σ_{ij} is standard deviation of the expert assessments of proposal “i” for criteria “j”. The quality indexes (QI) were obtained for the 150 proposals, 20 of which are presented in Table 5.

3.2.3. Prospective analysis of the demand

From the existing methods of prospective analysis, the present phase of the study implemented the Delphi consulting technique. Developed in the 1950s, the Delphi method serves as a process for technological forecasting: a procedure “to obtain the most reliable consensus of a group of experts...by a series of intensive questionnaires interspersed with controlled opinion feedback” (Dalkey and

Helmer, 1963). Although other methodologies have been developed ever since, it may be argued that the Delphi technique can produce superior results (Rowe and Wright, 1999). Furthermore, because this is the same technique as that applied to analyse the quality of the proposals, it was possible to perform the prospective analysis in conjunction with the proposals’ quality evaluation process. The evaluation experts had to provide a reasoned and agreed-upon forecast on the utility of education proposals with regard to the future needs of SMEs in the medium run (4 years). This would, amongst others, enable quantification of the “strategic fit” (Hale, 1995).

The application of this technique was also supported by the web platform for discussion. Again, the consensus criterion on the evaluations was that the deviation should be smaller or equal to 1. Once this was achieved, the index was calculated from the average of the valuations as follows:

$$PI(i) = \frac{4R_{High}(i) + 3R_{Medium}(i) + 3R_{Low}(i) + 1R_{Indifferent}(i)}{\text{Total number of answers}(i)}, \quad (4)$$

where $PI(i)$ is the prospective index of proposal “ i ”, R_{High} is the number of answers with option High. R_{Medium} is the number of answers with option MEDIUM. R_{Low} is the number of answers with option LOW. $R_{Indifferent}$ is the number of answers with option INDIFFERENT.

An index of similar characteristics is applied in the literature for measuring industrial prospective (Observatory of Technologic Industrial Prospective, 2005). This index works with a 4-point Likert scale and was used as reference for the construction of I_v . The final step consisted in the normalisation of the result to a scale of percentages to make it easier to understand.

3.2.4. Multicriteria integration

In line with the objectives of the project, the present demand, the demand in the medium run and the quality are the three criteria considered in the decision-making process. For each criterion, a quantitative index is defined, namely DI , PI and QI . The information is then integrated to produce a total ranking of education proposals, which will serve the project leaders (academic staff and administrators of the Valencia University of Technology), as a reference table from which to select those proposals which will ultimately be developed, produced in e-learning format and executed.

Multicriteria techniques to assist decision-making processes have been used in environmental applications for over two decades (an interesting study can be consulted in Brunner and Starkl, 2004). Many different techniques have been applied, of which the following two types are the most prominent (Lahdelma et al., 2000): (a) aggregation methods, such as the Weighted Sum, Multiattribute Theory, SMART and AHP; (b) outranking methods, especially ELECTRE (II, III and IV) and PROMETHEE (I and II).

According to definitions given by Roy (1996), the required ranking corresponds with the solution of a $P(z)$ multicriteria problem, in which the criteria represent the three indexes and the alternatives are the brief proposals. The simplest process to integrate the information of the three indicators would be the construction of an additive function (weighted sum). However, this procedure can hide information to the decision maker when it comes to generating the ranking. Outranking techniques enable more precise classification, based on a preferences' graph among alternatives and, from this, help the decision maker to determine the final ranking. From the techniques available, ELECTRE III allows weighting of the importance of each index within the set, and it also enables definition of the most flexible preference relations by means of the so-called pseudo-criteria (equivalent to a fuzzy logic model).

For the application, the experts were enquired via a semi-structured interview. The interpretation of their preferences gave way to the definition of the parameters of ELECTRE III:

- vector of weights of the criteria $\vec{\omega} = (\omega_{DI}, \omega_{PI}, \omega_{QI}) = (0.4, 0.2, 0.4)$;
- fuzzy parameterisation: constant values of strict preference ($p = 15\%$) and indifference ($q = 5\%$), zero value of the veto parameter ($v = 0$).

Normalisation is an essential procedure in some MCDM techniques. However, it is not necessary in some outranking methods as is the case of ELECTRE III. This facilitates the evaluation process and avoids problematic effects such as the well-known rank reversal (Vincke, 1992). In the present case study, the data of the three indicators are expressed in the same scale [0,100], in order to help the decision makers to understand the meaning of each index. In other future applications where this were not to be necessary, ELECTRE III would allow the combination of the three indexes expressed in different scales.

In order to verify the stability of the ranking obtained, a sensitivity analysis towards relative variations of 25% of the weight values was performed and so the ω -vector was varied within the following intervals:

$$\vec{\omega}^* = (\omega_{DI}^*, \omega_{PI}^*, \omega_{QI}^*) = ([0.2, 0.6], [0.1, 0.3], [0.2, 0.6]).$$

Table 5 shows the ranking obtained. It also presents the values of the proposals with respect to the three indexes as well as the most significant variations in the position of the proposals after the sensitivity analysis was performed. The results obtained from a weighted-sum-based integration of the three indexes are also shown. This additional analysis was carried out to substantiate the robustness of the Electre III. Eq. (5) was developed as an indicator for the robustness of the ranking obtained. For the case study, the values corresponding to the Electre III and the weighted-sum techniques respectively, were $Re_{QI} = 0.939$, $Re_{DI} = 0.924$, $Re_{PI} = 0.955$, $Rws_{QI} = 0.899$, $Rws_{DI} = 0.918$, $Rws_{PI} = 0.942$. These results confirm greater robustness of the Electre III in comparison to the weighted sum, where the larger the value of R , the greater the robustness, thus justifying its application in the methodology

$$Ra_b = 1 - \frac{\sum_{i=1}^n |A_{\max} p_i|}{(n^2/2)}, \quad (5)$$

where Ra_b is the indicator of robustness of the ranking, where a refers to the technique employed (e = Electre III and ws = Weighted Sum) and b to the index concerned (QI , DI and PI). $|A_{\max} p_i|$ is maximum variation of proposal “ i ”, n is the total number of proposals. $(n^2/2)$ is upper limit of $\sum_{i=1}^n |A_{\max} p_i|$.

3.2.5. e-Learning courses: design and production, execution and evaluation

After consideration of the total-ranking results, the decision makers employed the same experts who had made the selected proposals to conduct further work: this time, the experts were tasked with the design and production of

the courses in e-learning format. Because of the specific characteristics inherent in e-learning, the experts received pedagogic and technological assistance (Martínez et al., 2007; Govindasamy, 2002) throughout the entire process. In support of this decision was the practical experience which showed that some of the proposals prioritised in the study could not be developed because of two main reasons: (i) not all the experts were available for the planned period or (ii) the experts had difficulties to adapt to the peculiarities involved in e-learning. Given these conditions, and bearing the ranking information in mind, the project leaders decided on the courses to be produced and executed (Table 6). Most of the proposals embraced issues on environmental legislation, on economic and taxation matters, as well as glossaries of English terminology. Even though no explicit proposals existed under these names as such, these topics were regarded as basic and essential requirements and so it was decided to produce the courses 6, 10, 13 and 17. On the other hand, courses 3, 15 and 18 were created by grouping specific proposals belonging to one generic subject. Lastly, the decision taken on agricultural related courses 1, 8 and 14 was entirely intuitive (based on the importance of the agricultural sector in the Valencian Region) and was taken "out-of-methodology".

The Gantt diagram for the implementation of the methodology (Table 7) presents the temporal distribution of the tasks during the design and production phase of the methodology, as well as the human resources required.

As can be observed, this phase covered a period of 1 year, 7 months of which were dedicated to the studies and analyses necessary for decision making and 5 months to the production of the courses. All the tasks were coordinated by the Project Manager, who was assisted by an experienced coordinator in e-learning systems. The majority of the experts and personnel with specific qualifications were required for the generation and evaluation of proposals and for the production of the courses. Requirements for support staff were optimised and, as can be observed, most of them were assigned as direct support of the teaching staff during the production of the courses to aid principally in non-academic tasks such as the composition of texts, design of illustrations or animations and the resolution of bureaucratic procedures.

Subsequent to their production, the courses were executed. The exploitation period of a course includes the matriculation phase (application, selection and registration), the completion of the course via internet and an on-site written test to verify the students' identity and ensure their qualification. It was decided on a maximum of three annual editions per course because not only did the students study outside working hours, but it was also necessary to offer alternative exam dates. Furthermore, the availability of the teaching staff was limited and so it was vital to the programme success.

The last phase of the methodology concerns the assessment of the tuition of the courses. A survey was

Table 6
Courses performance data (after 2 years) ordered by successful certificates

Id	Course	E	Ap	Ad	C	S (%)	Sd (%)
20	Environmental management systems	6	827	222	176	73.53	78.46
23	Integrated systems of quality and environmental management	6	864	224	176	74.85	80.94
4	Environmental management systems audits	6	790	194	162	78.17	79.33
11	Renewable energies: solar and wind power	6	675	190	146	76.70	85.71
12	Treatment of industrial liquid effluents	5	502	154	115	76.30	80.92
21	Geographic information systems applied to natural resource management	4	526	137	103	70.87	79.97
3	Environmental aspects of urban, industrial and building infrastructure	3	432	99	88	75.35	80.51
13	Technical english for environmental issues	3	465	99	77	69.73	71.21
7	Remediation and minimisation of acoustic impacts	2	462	76	64	74.85	77.47
17	Environmental legislation	2	340	68	63	75.50	83.41
22	Remote sensing systems for the prevention of environmental hazards	2	451	71	56	72.25	74.01
18	Environmental chemistry for industrial processes	2	305	60	55	75.00	77.13
2	Environmental aspects of air pollution	2	413	64	54	76.57	78.93
19	Health and safety at work, the environment and quality	2	297	61	47	73.50	80.44
24	Tourism and the environment	2	347	59	47	75.47	80.00
9	Respectful product design and development	2	244	60	45	75.50	83.00
5	Characterisation and assessment of acoustic environmental impact	2	264	60	43	72.40	77.36
16	Environmental impact assessment methodology	2	295	55	43	78.50	80.23
10	Economics and the environment	1	284	38	38	82.10	91.97
8	Soil degradation and recovery	1	267	30	30	67.00	67.54
1	Agriculture and the environment	1	128	31	23	87.50	93.36
6	Environmental accounting and taxation for the small-and medium-sized enterprise	1	113	28	23	77.50	87.36
15	The environment and urban quality	1	145	35	23	68.50	69.20
14	Sustainable measures and techniques of soil conservation	1	235	27	15	73.70	77.29

E, editions; Ap, applications; Ad, Admittances; C, certificates; S, global student satisfaction; Sd, student satisfaction of course design.

Table 7
Gantt diagram

Methodology		Time (months)												Human resources			
Phase	Task	J	F	M	A	M	J	J	A	S	O	N	D	C	E		A
Demand analysis	Design and dispatch of survey	■												1	2		2
	Compilation of data	■	■											1			2
	Statistical analysis			■										1	2		2
Supply analysis	Design of the proposals' format	■												1			
	Selection of experts for proposal generation	■												1			
	Generation of proposals		■	■										1	25		1
	Supervision of proposals		■	■										1	2		
	Selection of experts for proposal evaluation		■											1	2		
	Web-based Delphi assessment													1	15		2
	Multicriteria assessment				■									1	3		1
Prospective analysis	Conclusions					■	■							1	3		1
	Selection of experts for evaluation													1	2		
	Web-based Delphi assessment		■											1	15		2
	Conclusions				■		■							1	3		1
Multicriteria integration	Calculation of indexes							■						1	2		
	Integration of indexes							■						1	2		
	Sensitivity analysis							■						1	2		
	Ranking of proposals							■						1	2		
Production	Adaptation of proposals							■							2		1
	Confirmation of expert availability							■						2			1
	Production decision							■						2			
	Hiring of teaching staff							■						1			1
	Production of the courses							■						2	65		26
	Pedagogic supervision							■						1	3		1
	Academic supervision							■						2	2		1
	Course set up on the web platform													2	1		2

C, coordinator; E, expert; A, administrative.

Table 8
Items of the course satisfaction survey

List of propositions	
A	The organisation of the course has been good
B	The contents have been correctly developed during the course
C	I am satisfied with the content of the didactic material of the course
D	The didactic materials of the course are user-friendly
E	I believe the teaching methods used are adequate
F	I regard the evaluation system as effective
G	I believe the activities proposed are adequate
H	I think the tutor dominates the contents of the course
I	The tutor has quickly responded to my queries
J	The tutor has efficiently resolved my doubts
K	Technical problems I encountered with the Internet were attended to
L	The information media employed are adequate
M	I believe group discussions via web stimulate student participation on the course
N	This course was perfectly adapted to my learning pace
O	The education received is related to the job
P	From my experience, I recommend this course to others
Q	My expectations have been satisfied
R	I think e-learning is a convenient type of professional improvement
S	I believe the use of Internet in education presents more advantages than inconveniences
T	In general, I am satisfied with the result of the course

designed with the aim of evaluating the level of satisfaction among the students. Anonymity of opinions was guaranteed. The survey was filled in by those students who had finished and successfully passed the course, and it could easily be completed by means of a specific on-line tool. The items of the survey are presented in Table 8.

4. Results

The previous section presented the results corresponding to the generation and evaluation of the proposals. This section will address the results of the courses' performance within the first 2 years of operation. These are exhibited in Table 6, which shows the present demand for the courses, as well as the results of the surveys on student satisfaction. It should be noted that not all the courses were able to reach the maximum number of annual editions. As can be observed, this was not due to a lack of demand, rather a lack of available teaching staff. Nevertheless, the general results can be considered satisfactory with a total of 1712 students obtaining certification, and satisfaction indexes being superior (in mean values) to 70%. The demand was 4.51 times greater than the number of finally registered people. The drop-out percentage was a mere 20.07%, which lies within the lower limit of the e-learning drop-out range cited by Frankola (2001). Finally, it should be emphasised that the students who completed the courses worked in 1440 different SMEs of the Valencian Region

and hence the impact of the training programme on the business sector can be considered of significant importance.

5. Discussion

The application of the proposed methodology reveals the importance of the tools and techniques used for the development of the tasks involved. In fact, the effectiveness and efficiency of the methodology rely on the correct selection of those tools and techniques that will most adequately suit both the economic resources available and the temporal planning of the project. In this sense, the experience drawn from the case study enables evaluation of the performance of the adopted solutions.

5.1. On technique performance

A qualitative analysis of the demand using techniques of multivariate analysis is fully justified. The information obtained facilitates the process of search into potential courses, because it allows reducing the number of possible environmental fields in question. From a pedagogic point of view, it assists in the selection of the didactic strategy most suited to the learner (Conole et al., 2004). Performing a qualitative analysis also helps to foresee the difficulties involved in the e-learning modality, as was the case for the course "Tourism and the Environment". The analysis revealed that students of this particular course showed special aversion towards the use of computers for educational purposes and so it was considered opportune that these students be supervised more closely than students of other courses. Consequently, although carrying out a qualitative analysis could be a complex task, the effort it requires is offset by the benefits it yields. In the same way, the quantitative demand indicator has proven to be a good pointer for the real demand of the executed courses as the number of applications run parallel to the results of the analysis of expected demand.

5.2. On indicator performance

The prospective demand indicator and the quality indicator have also shown to be useful and effective. The influence of the information revealed by the "forecast" indicator was the determining factor in the decision to carry out the course on "Renewable Energies: Solar and Wind Power" which obtained a high real and growing demand even though the other indicators had predicted worst results. The quality index was an equally accurate measure. The satisfaction results obtained by the courses correspond to the ex ante evaluation of their quality. In fact, the approval shown by the students on the quality of the design of the courses and of the materials is superior to the average value of the global evaluation of the course (Table 6). In any case, although this indicator guarantees a high academic level, it fails to account for any possible reluctance within the staff towards producing e-learning

materials. This is a factor that decision makers are forced to consider even though it is not made explicit in the general methodology.

The integration of information of the three indicators via the ELECTRE III technique provides a reliable ranking on which to base decisions. In addition to the individual validity of the indicators referred to above, is the priority given to those alternatives which show equilibrated values of the three indicators. This is a particular characteristic of the outranking techniques. These techniques are recommended over other multicriteria techniques for their capability to detect unbalanced decision alternatives, where an imbalance is an undesirable situation in this methodology (Roy and Bouyssou, 1993). An equally important factor reinforcing the reliability of the ranking over other possibilities is the stability of the technique's result with respect to the sensitivity analysis that was carried out.

5.3. On time and costs

The 7 months required to carry out all the analyses necessary prior to the production of the courses can seem, in principle, disproportionate when compared to the 5 months dedicated to the production phase. But bearing in mind that the aim of the methodology is to secure the success of the courses for a minimum period of—at least—4 years, the time dedicated to the analysis should not be regarded as excessive, as long as the conclusions can help to make the right decisions. Moreover, the experience was a novel one for those responsible as well as for the participants, which can help to explain the fact that reaction times are superior to those expected at the saturation point of the learning curve. In this case, it is estimated that the time can be reduced by 50% from 7 months to 14 weeks, even though it has not been possible to corroborate this datum with an entire experience. The case study indeed verified that once the participants have gained experience in the process, the web Delphi discussion time can be reduced from an initial 50 days to a final 20 days. Further positive externalities experienced from e-learning include the reduction of the time necessary for travelling to and from the education site in face-to-face education (Crompton et al., 2002), and the possibility of direct and en masse reutilisation of educational material. Lastly, it is necessary to note that the costs of production of e-learning courses have been similar to those corresponding to face-to-face education, in strictly monetary terms. Nevertheless, the e-learning modality contributes to greater time flexibility—a factor which is critical in training programmes for SME workers.

On the cost, needless to say that the methodology proposed represented less than 1% of the total investment on the project.

6. Conclusions

To date, the benefits drawn from sustainable “behaviour” are being more and more understood and the

importance of close and effective collaboration between SMEs and the environment is becoming ever more evident. Environmental education and training represents an essential component of this process (Viloria, 1991).

The purpose of this article was to present a robust and applicable methodology to aid in the decision-making process of potential environmental training programmes directed at SME workers. It was important that the resulting courses respond to present as well as to prospective demand, and that they prove to be of sufficient quality to satisfy the students involved. As stated by Venselaar (1995), “*the value of good postacademic study possibilities cannot be stressed enough!*” The results from the case study have shown that the methodology proposed is capable of meeting these objectives. The approach provided decision makers with information of high value added and a two-way success was recorded: there was a large demand for the courses summed to a favourable degree of student satisfaction.

The costs incurred in the application of the methodology were also considered satisfactory. These accounted for less than 1% of the project's global budget. A percentage which can be reduced as the methodology becomes more familiar to its users. Because of the potential to reduce costs, and given the economic implications of decision errors, the effort put into the allocation of resources at the various stages of the project is fully justified. What is more, it should be noted that the issue “cost reduction”—“effort” is only relevant for the design of educational programmes of great scope as in this case study of regional scale. Consequently, the net result derived from the application of the methodology will seek to push for a reduction of costs and an increase in the overall satisfaction of the different social actors involved.

Table 2 presents the 19 areas of environmental priority in order of preference as indicated by the SMEs involved in the case study. It is interesting to note that the most favoured areas are precisely those which concern everyday problems to SME workers, such as environmental technology and management, whereas problems which are of specific importance to the Valencian region as a whole, namely tourism and the environment as well as the landscape, are less favoured. Further analysis is required to study ways to explain and reduce if possible the existent gap between SME wants and regional needs.

At this point, the authors consider it important to mention that during the execution of the courses, it was precisely those decisions taken “out-of-methodology”, such as the production of the courses “Agriculture and the Environment”, “Sustainable measures and techniques of soil conservation” or “Soil degradation and recovery”, which achieved lower real demand. This observation corroborates positively with the result forecasted by the methodology hence demonstrating that the decisions taken on these particular courses were based on intuitions which proved to be inconsistent, and so it is concluded that the proposed methodology is a rigorous and valid reference for

the design and execution of environmental education programmes.

Even though the methodology has been successful, there exist some weaknesses and several suggestions for improvements. One of the limitations of the approach lies in that the evaluation of the “brief proposals” relies solely on the quality factor. Integrating other quantitative measures relevant to the problem such as the ones to determine the difficulties experienced by the staff with the particularities inherent in e-learning, could have strengthened the results (Sinclair and Diduck, 2001). Similarly, it is considered beneficial for future works to explore the incorporation of qualitative information into the demand index. Finally, it is important not to limit the ex post evaluation of environmental education to a student satisfaction survey (Garavalia and Gredler, 2004). The authors thus propose developing specific studies about indicators for the real impact of environmental education on the socio-economic environment. For the case study exposed, the research would be centred on the topics of greatest real and future demand: (i) integrated systems, and quality and environmental audits, (ii) renewable energies and (iii) technologies for treatment of industrial residues. In this respect, an advance in the indicators to be studied would be, respectively, (i) the evolution of the number of SMEs certified in accordance with the ISO 14,000 norms, (ii) the number of alternative energy systems installed and maintained by internal workers and (iii) investment of SMEs in technologies for the treatment of pollutants. All things considered, an inclusion of these improvement means into the methodology would further facilitate and reinforce the decision-making process of environmental e-learning programmes.

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Efficiency of removal of cadmium from aqueous solutions by plant leaves and the effects of interaction of combinations of leaves on their removal efficiency

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Abstract

Removal of cadmium from aqueous solutions using 20 species of plant leaves and combinations of these leaves have been studied. Several factors affecting the removal efficiency have been studied. The most efficient types of plant leaves for the removal of cadmium are those of styrax, plum, pomegranate and walnut. The interaction effect of the combined leaf samples on the efficiency of removal of cadmium has been found to be additive in combinations involving styrax plant leaves but seems to be antagonistic in all other combinations. The optimum experimental conditions for removal of cadmium have been found to be at pH 4.1, using high concentrations of naturally dried plant leaves, using ground leaves and to remove cadmium from agitated aqueous solutions. The percentage of metal removed at an initial cadmium concentration of 10 mg/l by the most efficient types of leaves have been found to be 85% for styrax leaves, 85% for plum leaves, 80% for pomegranate leaves, 78% for walnut leaves and 77% for meddler leaves. The presence of foreign ions or complexing agents has been found to reduce the efficiency of removal of cadmium by plant leaves. About 80–85% of the cadmium in charged plant leaves has been released under the influence of changing the pH of the solution, addition of competing ions and the addition of EDTA. The results of removal of cadmium by plant leaves have been found to follow the Freundlich adsorption isotherm, first-order reaction with respect to cadmium and to have intra-pore diffusion as the rate-limiting step.

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Keywords: Cadmium; Removal; Plant leaves; Interaction; Efficiency; Kinetics; Aqueous solutions

1. Introduction

Cadmium is one of the most toxic metals affecting man, animals and plants (Friberg et al., 1974; Brooks, 1978; Ormrod, 1984). It was considered one of the “priority pollutants” by the EEC countries (Barbur, 1983). Its excretion from the body is very low (Friberg et al., 1974) and it has synergistic toxicity with other metals, for example, with zinc (Cheremisinoff and Habib, 1972). Thus the removal of cadmium from polluted water is of great importance. Only very few studies have been done on the level of cadmium in the environment of the West Bank, Palestine. One of these studies showed the concentration

of cadmium in soil of the highway between Ramallah and Nablus in the West Bank to be 0.45 µg/g (Swaileh et al., 2001a). The concentration of cadmium in the leaves of six common types of roadside plants around the highway of Nablus–Ramallah was reported in the range of 0.3–0.86 µg/g (Swaileh et al., 2001b). Land snails were reported to magnify cadmium concentration to an average of 19.4 µg/g total dry weight of land snail *Levantina hierosylima* taken from four locations in the West Bank, Palestine (Swaileh et al., 2001b).

Several sorbents have been suggested in the literature for the removal of toxic metals (including cadmium) from water. These include activated carbon (Ferro-Garcia et al., 1988), fly-ash (Yadava et al., 1987), zeolite (Kesraouioui et al., 1994), ferrites (Navratil, 1994) and limestone (Chen et al., 1999). The most commonly used sorbent is activated

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carbon, which requires regeneration and is costly. Several low-cost sorbents of agricultural and biological origin have been suggested for the removal of toxic metals from polluted waters. Examples of these sorbents are hair (Wilhelm et al., 1989), starch-xanthate (Chaudhari and Tare, 1996), tea-leaves (Singh et al., 1993), apple residues (Lee et al., 1998), hop (Torresdey et al., 2002), moss (Al-Asheh and Duvnjak, 1997), Duckweed (Ornes, 1994), seaweeds (Aderhold et al., 1996), bacteria (Zouboulis et al., 2004), algae (Gin et al., 2002) and fungal biomass (Kapoor and Viraraghavan, 1998).

Due to the availability and low cost, plant leaves were considered as an efficient sorbent for the removal of metal ions from polluted water. Their efficiency was close to the activated carbon results. Examples of reported efficient plant leaves for the removal of metal ions are reed for the removal of cadmium (Sayrafi et al., 1996), sage for cadmium and zinc (Abu-El-Halawa et al., 2003), neem for lead (Bhattacharyya and Sharma, 2004), *Eucalyptus* L. for lead and cadmium (Salim and Abu-El-Halawa, 2002), poplar for the removal of lead (Salim et al., 1994) and copper (Al-Subu et al., 2001), walnut for zinc (Salim et al., 2003), oleander for lead and copper (Abu-El-Halawa et al., 2003), pine for nickel (Salim, 1988) and cypress for aluminum (Salim and Robinson, 1985).

The interaction effects of combinations of cinchona, cypress and pine leaves were studied for the removal of lead from aqueous solutions (Al-Subu, 2002). The interaction effect of plant leaves has been reported to be additive in some combinations, for example, pine and cypress combinations, and antagonistic in other combinations, for example, cinchona with cypress or with pine leaves.

In this study, we compared the efficiency of different types of leaves that are common in Palestine for removing cadmium ions from aqueous solutions. The interaction effect of combinations of the most efficient leaf types has been studied on the removal process of cadmium. Several factors affecting the removal process have been studied. Applicability of adsorption isotherms on the removal process has been tested and a few kinetic parameters of the removal process will be determined. The release of cadmium ions from saturated plant leaves will also be studied.

2. Materials and methods

Samples of 20 common types of plant leaves were gathered from the north areas of the West Bank, Palestine. The various types of plant leaves and their locations are listed in Table 1. Leaves were cleaned thoroughly with deionized water, dried in an oven at 70 °C until constant weight was achieved, after which the leaves were sieved into constant size (0.6–0.7 mm pore radius) and then kept in small bags for further use in the experiments. All experiments were done using oven-dried and ground leaves unless otherwise stated. All types of leaves used were free from cadmium, as indicated from the negligible

Table 1
Plant species studied and their collection sites

Scientific name	Common name	Location of collection
<i>Ficus carica</i>	Fig tree	Jenin
<i>Amygdalus communis</i>	Almond	Jenin
<i>Maspilus japonica</i>	Japanese medlar	Jenin
<i>Prunus armeniaca</i>	Apricot	Jenin
<i>Prunus domestica</i>	Plum	Qalqilia
<i>Morus alba</i>	Mulberry	Jenin
<i>Juglans regia</i>	Walnut	Nablus
<i>Punica granatum</i>	Pomegranate	Jenin
<i>Olea europaea</i>	Olives	Jenin
<i>Malus sylvestris</i>	Apple	Jenin
<i>Ceratonia siliqua</i>	Carob	Jenin
<i>Eucalyptus camaldulensis</i>	Eucalyptus	Jenin
<i>Styrax japonicus</i>	Styrax	Jenin
<i>Quercus calliprinos</i>	Oak	Jenin
<i>Pistacia palestina</i>	Palestine pistachio	Jenin
<i>Vitis vinifera</i>	Vine	Jenin
<i>Pinus halepensis</i>	Pine	Jenin
<i>Citrus sinensis</i>	Orange	Jenin
<i>Citrus limon</i>	Lemon	Jenin
<i>Cupressus semervirenes</i>	Cypress	Jenin

concentrations of cadmium leached from leaves having about the same leaf-concentrations used in this work after soaking in 1 M HNO₃ for 3 days. Used polyethylene bottles (250 ml) were used in this work. This type of containers was reported by several authors to have minimum adsorption on the container surfaces (King et al., 1974). Only negligible amounts of cadmium were found experimentally adsorbed on the container surfaces under the conditions used in this work. The containers used were decontaminated from metal ions by soaking in 1 M HNO₃ for 3 days and then cleaned thoroughly with deionized water before being used.

Cadmium solutions used in this work were prepared by dilution from a 1000 mg/l stock solution prepared from analytical grade Cd(NO₃)₂·4H₂O. All other chemicals used were of high-grade purity.

Removal of cadmium by leaves was measured by following the decrease of concentration of cadmium from 200 ml buffered cadmium solutions on 12 g/l leaves. Concentrations of combinations of leaves used were always divided equally between the types of leaves forming the combined samples of plant leaves. The desired mass of the studied plant leaves was added to a polyethylene bottle containing 200 mL acetate buffer solution. To this suspension of plant leaves, an exact amount of cadmium stock solution (1000 mg/l) was added using Oxford pipette. For the analysis of cadmium concentration in the leaf suspension, an aliquot of 0.5 ml of the sample solution was added to a thermostatic (22 ± 1 °C) cell containing de-aerated 5.0 ml of the acetate buffer. Clear solutions were obtained from the leaf suspensions by using a small glass tube with a sintered glass disk. The removal of cadmium by plant leaves was always followed until equilibrium was attained. The time required for equilibrium was different from one

type of leaves to another and was in the range of 48–190 h. The analytical method used for the determination of cadmium concentrations in solution was the differential anodic stripping voltammetry (DPASV) using a Polarographic Analyzer Stripping Voltammeter Model 264 B, EG&G Instrument. The other working conditions of the instrument are listed in Table 2. The concentration of cadmium in solution was calculated by comparing the obtained peak area with peak areas obtained for standards plotted on calibration curves. The standard addition method was used once every 5–7 measurements in order to check the applicability of the calibration curve. The method of DPASV has the advantage of having very high sensitivity and very low detection limits that makes it a good choice for the analysis of dilute solutions of some metals, including cadmium.

Solutions were buffered at pH 4, unless otherwise stated, using acetate buffers. The pH values of solutions were measured using a pH-meter JENWAY, type 3310. The exact pH was obtained by the addition of drops of $\sim 1\text{ M}$ HNO_3 or NaOH , as required.

Three readings were taken for each sample and the average was reported. The relative deviation of the measured values was normally $\sim 5\text{--}7\%$; deviated results of $\geq 10\%$ were discarded.

The reliability of the obtained results was tested by applying the MANOVA multi-variate analysis of variance statistical program on five repetitions of removal experiments done using three types of leaves and their combinations (examples of the repetitions taken for the removal of cadmium on plant leaves are shown in Table 3). The results of the statistical analysis indicated no significant difference at $\alpha = 0.05$. The F values obtained for the experimental results (0.201 and 0.230 for the styrax–plum and styrax–plum–walnut leaf combinations) were less than the critical

F values (4.000) at $\alpha = 0.05$. The obtained p values were 0.989 for the styrax–plum combination and 0.987 for the styrax–plum–walnut plant leaf combination. The pair-wise comparison of the mean values of the repeated experimental groups indicated no significant difference at $\alpha = 0.05$.

3. Results and discussion

3.1. Effect of type of leaves

Removal of cadmium from aqueous solutions was studied using 20 types of plant leaves. The results obtained are shown in Table 4. Activated carbon is also included in the table for the sake of comparison. The obtained results indicate that:

1. The efficiency of plant leaves for the removal of cadmium from aqueous solutions differs highly from one type to another.
2. The efficiency of some types of leaves (e.g. styrax leaves) is high and close to the efficiency of activated carbon for the removal of cadmium.
3. The time required to reach maximum removal of cadmium (i.e. equilibrium time) varies highly from one type of leaves to another. This equilibrium time is probably related to the shape and to the strength of the leaf surface. This equilibrium time is, e.g., 48 h for rough fig leaves but 190 h for the smooth and solid surface of oak leaves.
4. The efficiency for the studied plant leaves and carbon to remove cadmium from aqueous solutions can be arranged in the decreasing order:

Activated carbon > styrax > plum > pomegranate > walnut > medlar > cypress > mulberry > carob > olive > eucalyptus > pistachio > almond > vine > fig > apricot > oak > pine > apple > orange > lemon leaves. The styrax leaves are the most efficient and the lemon leaves are the least efficient types of plant leaves.

The first five efficient types of leaves have been used to study the effect of most of the factors studied in this work.

The maximum efficiencies, reported in previous studies, for the removal of cadmium from aqueous solutions by plant leaves were $\sim 95\%$ from 1 mg/l Cd solution by 20 g/l reed leaves (Sayrafi et al., 1999), $\sim 99\%$ from 2.2 mg/l Cd solution by 50 g/l sage leaves (Abu-El-Halawa et al., 2003), $\sim 85\%$ from 4.6 mg/l Cd solution by 33.3 g/l eucalyptus leaves (Salim and Abu-El-Halawa, 2002) and $\sim 40\%$ from 1.7 mg/l Cd solution by 5.4 g/l beech leaves (Salim et al., 1992). The results of the present work show a maximum efficiency of removal of 94% of cadmium from 5.0 mg/l cadmium solution by 24 g/l styrax leaves at pH 4.0 (see Section 3.4). This efficiency is competitive with the previously reported maximum efficiencies of plant leaves for the removal of cadmium from aqueous solutions.

Table 2

Working conditions used for the differential pulse anodic stripping voltammetry

Experimental parameter for low and moderate concentration

Working electrode	Mercury drop electrode
Drop size	Middle
Reference electrode	Ag/AgCl electrode
Auxiliary electrode	Pt wire
Initial potential	-0.85 V
Final potential	-0.5 V
Deposition potential	-0.85 V
Integration set point	-0.63 V
Purge time	0.5 min
Deposition time	70 s ^a
Equilibrium time	15 s
Scan rate	10 mV/s
Current	1 μA
Pulse amplitude	25 mV
Recorder x-axes scale	500 mV/cm ^b
Recorder y-axes scale	250 mV/cm

^aDeposition time for high concentrations was 30 s.

^bRecorder x-axes scale for high concentrations was 100 mV/cm.

Table 3

Repetitions of results of experiments on the removal of cadmium on samples of combined styrax and plum leaves and of combined styrax, plum and walnut (in equal weight ratio) plant leaves

T/h	C _i	T/h	C _i	T/h	C _i	T/h	C _i	T/h	C _i
Styrax and plum leaves									
0.5	10.42	0.5	10.50	0.5	10.31	0.3	10.01	0.3	11.21
1.0	8.91	0.5	9.01	1.5	8.30	0.5	8.31	1.0	8.51
3.0	8.31	1.0	6.71	3.0	8.12	1.0	7.01	2.0	8.32
5.0	7.61	3.0	6.42	5.0	7.22	3.0	6.82	3.0	7.82
10.0	6.71	5.0	6.62	10.0	6.51	5.0	6.62	5.0	7.31
24.0	6.22	10.0	6.82	15.0	5.90	10.0	7.01	10.0	7.11
48.0	6.40	24.0	7.31	24.0	6.41	15.0	7.11	24.0	6.71
72.0	6.60	48.0	7.31	48.0	6.52	24.0	7.32	48.0	7.02
96.0	6.71	72.0	7.51	53.0	6.80	48.0	7.02	72.0	7.30
120	6.60	95.0	7.20	72.0	6.61	72.0	6.41	96.0	6.90
144	6.50	120	6.70	96.0	6.22	96.0	6.52	120	6.60
168	6.41	144	6.72	120	6.10	120	6.41	144	6.21
196	6.42	168	6.41	144	6.01	144	6.41	168	6.41
216	6.31	192	6.41	192	5.91	196	6.32	216	6.11
240	6.31	240	6.12	240	5.70	240	6.32	240	6.02
Styrax, plum and walnut leaves									
0.5	8.12	0.5	10.80	0.5	10.42	0.5	8.60	0.5	10.31
1.0	7.11	1.0	8.40	1.0	8.31	1.0	7.31	1.0	7.40
1.5	6.41	1.5	6.51	1.5	6.82	1.5	7.01	1.5	7.02
3.0	6.30	3.0	6.31	3.0	6.61	3.0	6.70	3.0	6.82
5.0	6.50	5.0	6.72	5.0	6.40	5.0	6.90	5.0	7.30
15.0	7.10	15.0	7.21	15.0	6.81	15.0	7.20	15.0	7.11
20.0	6.61	20.0	7.32	20.0	7.01	20.0	7.22	20.0	7.21
48.0	6.72	48.0	7.82	48.0	7.11	48.0	7.31	48.0	7.70
51.0	7.11	51.0	7.72	51.0	7.22	51.0	7.51	51.0	8.20
72.0	7.22	72.0	8.00	72.0	7.61	72.0	8.31	72.0	8.42
96.0	7.50	96.0	7.90	96.0	8.10	96.0	8.51	96.0	8.41
120	8.10	120	7.40	120	8.40	120	8.12	120	8.10
144	8.20	144	7.21	144	8.21	144	7.92	144	7.72
196	7.81	196	7.11	196	7.40	196	7.41	196	7.52
240	7.51	—	—	240	7.02	240	7.21	240	7.41

Concentration of Cd = 20 mg/l; concentration of leaves = 15 g/l; C_i: concentration of cadmium ions (mg/l) found in solution after removal process. T/h: time/hour.

3.2. Interaction effects of combinations of plant leaves

Various combinations, in equal weight ratios, of the five most efficient types of plant leaves were used for removing cadmium from aqueous solutions. The results obtained are shown in Table 5. These results indicate that:

1. All combinations involving styrax leaves with other types of leaves showed efficiencies of removal almost the same as the efficiency of removal caused by styrax leaves alone.
2. All other combinations of plant leaves show a small antagonistic effect on the removal of cadmium.
3. None of the combinations studied show synergistic effect on the efficiency of removal of cadmium from aqueous solutions.

3.3. Effect of concentration of cadmium

The effect of concentration of cadmium from its solutions was studied using styrax plant leaves. The

results obtained are shown in Fig. 1. These results indicate that:

1. Removal processes of cadmium by plant leaves from the various concentrations of cadmium followed one pattern. In this pattern, the removal of cadmium was somewhat rapid in the first few hours (~50% of the removed cadmium occurs in the first 10 h). The removal process then slows down until it becomes almost steady after a long time (48–190 h, depending on the type of plant leaves used).
2. The time after which the removal rate slows down depends on the concentration of cadmium in solution. This time is shorter from dilute cadmium solutions than from more concentrated ones.

3.4. Effect of concentration of leaves

Removal of cadmium from cadmium solutions, 5.0 mg/l, was studied using several concentrations of the five most efficient types of leaves studied in this work. The results

Table 4
Effect of different plant leaves on the removal of cadmium

Type of leaves	Equilib. time (h)	Initial conc. of Cd (mg/l)					
		1.0	2.0	3.0	4.0	6.0	10.0
		Fraction of Cd removed					
Fig tree	48.0	0.56	0.58	0.58	0.59	0.61	0.63
Almond	72.0	0.60	0.61	0.63	0.63	0.63	0.64
Medlar	96.0	0.72	0.72	0.74	0.74	0.76	0.77
Apricot	72.0	0.56	0.56	0.55	0.57	0.58	0.61
Plum	72.0	0.80	0.81	0.82	0.82	0.84	0.85
Mulberry	48.0	0.66	0.68	0.67	0.70	0.71	0.71
Walnut	96.0	0.75	0.76	0.76	0.76	0.76	0.78
Pomegranate	72.0	0.76	0.78	0.77	0.78	0.79	0.80
Olives	120.0	0.64	0.66	0.67	0.68	0.68	0.72
Apple	72.0	0.48	0.48	0.51	0.51	0.52	0.55
Carob	120.0	0.65	0.67	0.68	0.69	0.70	0.71
Eucalyptus	48.0	0.62	0.64	0.65	0.66	0.67	0.72
Styrax	120.0	0.82	0.82	0.82	0.84	0.84	0.85
Oak	190.0	0.52	0.52	0.55	0.58	0.59	0.61
Pistachio	72.0	0.60	0.61	0.62	0.63	0.64	0.66
Vine	72.0	0.58	0.60	0.61	0.62	0.62	0.64
Pine	48.0	0.52	0.53	0.54	0.53	0.61	0.65
Orange	190.0	0.46	0.46	0.47	0.48	0.49	0.49
Lemon	190.0	0.39	0.40	0.44	0.47	0.49	0.58
Cypress	48.0	0.69	0.70	0.73	0.74	0.75	0.77
Activated carbon	48.0	—	—	—	0.88	—	—

Concentration of leaves = 12.0 g/l; pH = 4.0. Concentration of activated carbon = 12.0 g/l; pH = 4.0.

obtained indicate that the removal efficiency of cadmium is strongly affected by the concentration of leaves in solution. For example, the concentration of cadmium removed from 5 mg/l cadmium solutions, at pH 4.0, was 3.20, 3.35, 3.45, 3.55 and 3.35 by 4 g/l plant leaf suspension of medlar, pomegranate, plum, styrax and walnut leaves, respectively.

The concentration of cadmium removed from 5 mg/l cadmium solutions, at pH 4.0, was 4.45, 4.60, 4.65, 4.70 and 4.45 by 24 g/l plant leaf suspensions of medlar, pomegranate, plum, styrax and walnut leaves, respectively.

3.5. Effect of pH

The removal of cadmium from 2.0 mg/l aqueous cadmium solutions using the five most efficient types of leaves was studied at several pH-values ranging between 1 and 10. The pH values of solutions were obtained by the addition of ~1 M HNO₃ or NaOH, as required. The results obtained for the removal of cadmium, after equilibrium is attained, are shown in Fig. 2. These results show a high dependence of the removal process on the pH. The optimum pH value for obtaining the maximum efficiency of removal of cadmium by the studied leaves is pH 4.1. High pH values (>7) also resulted in an increase in the efficiency of removal of cadmium, but to a slightly less extent than from solutions of pH 4.1.

Cadmium is present in solutions of low pH values as free Cd²⁺ ions. At high pH values (>8 according to

Table 5
Interaction effect of several combinations of plant leaves on the removal of cadmium

Sample	Initial Cd concentration (mg/l)						
	0.5	1.0	1.5	3.0	5.0	7.0	10.0
	Fraction of Cd removed						
Styrax (1)	0.81	0.82	0.83	0.83	0.84	0.85	0.86
Plum (2)	0.79	0.80	0.81	0.82	0.83	0.85	0.85
Pomegranate (3)	0.75	0.76	0.77	0.77	0.78	0.79	0.80
Walnut (4)	0.74	0.74	0.75	0.76	0.77	0.78	0.78
Medlar (5)	0.72	0.73	0.73	0.74	0.75	0.76	0.77
1+2	0.80	0.81	0.82	0.83	0.83	0.84	0.85
1+3	0.76	0.77	0.77	0.78	0.80	0.82	0.83
1+4	0.77	0.77	0.78	0.80	0.81	0.82	0.83
1+5	0.74	0.75	0.76	0.78	0.80	0.81	0.82
2+3	0.76	0.77	0.77	0.78	0.79	0.81	0.82
2+4	0.74	0.75	0.76	0.77	0.78	0.79	0.81
2+5	0.74	0.75	0.76	0.76	0.77	0.78	0.80
3+4	0.73	0.73	0.74	0.75	0.76	0.77	0.78
3+5	0.72	0.73	0.73	0.74	0.76	0.77	0.79
4+5	0.70	0.70	0.70	0.72	0.72	0.73	0.75
1+2+3	0.77	0.80	0.78	0.79	0.81	0.82	0.84
1+2+4	0.74	0.74	0.74	0.76	0.79	0.81	0.82
1+2+5	0.72	0.72	0.72	0.75	0.77	0.78	0.81
1+3+4	0.75	0.76	0.77	0.78	0.80	0.81	0.83
1+3+5	0.71	0.71	0.71	0.73	0.75	0.76	0.79
1+4+5	0.72	0.72	0.72	0.74	0.76	0.78	0.80
2+3+4	0.74	0.75	0.76	0.77	0.78	0.79	0.81
2+3+5	0.70	0.70	0.69	0.72	0.74	0.75	0.79
2+4+5	0.71	0.72	0.72	0.73	0.75	0.76	0.78
3+4+5	0.70	0.70	0.71	0.72	0.75	0.77	0.80
1+2+3+4	0.77	0.78	0.79	0.80	0.82	0.83	0.84

Concentration of leaves = 12.0 g/l; pH = 4.0.

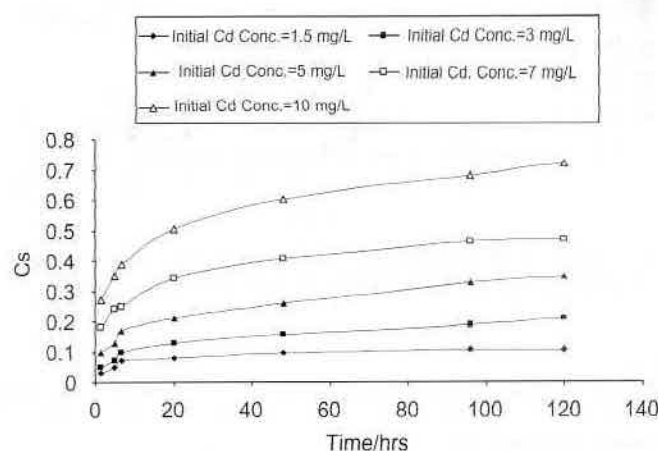


Fig. 1. Effect of concentration of cadmium on its removal from solution by styrax plant leaves. Concentration of leaves = 12.0 g/l, pH = 4.

Cordero et al., 2004) poorly soluble hydroxyl Cd(OH)₂ and Cd(OH)₃⁻ are formed.

The effect of pH on the removal capacity of cadmium below pH 4.1, in the present work, might be attributed to competition between cadmium and hydrogen ions on the adsorption sites of plant leaves. The hydrogen ion is a strong competitor for adsorption because of its small size.

The reduced capacity of adsorption of cadmium beyond pH 4.1 is probably due to the formation of cadmium complexes with organic components leached from the plant leaves. These complexes have larger sizes than free cadmium ions and thus are weaker competitors for adsorption.

The high removal capacity beyond pH 7 is due to the precipitation of cadmium from solution as cadmium hydroxide.

The maximum biosorption capacity by *Fucus spiralis* nonliving macro-alga was reported at pH $\approx$ 4.5 (Cordero et al., 2004). Removal of cadmium, using plant leaves, was recommended to be from aqueous solutions with pH values of $\sim$ 7 for the removal of cadmium by reed and sage plant leaves (Sayrafi et al., 1999; Salim and Abu-El-Halawa, 2002) and pH 5 using beech leaves (Salim et al., 1992).

3.6. Effect of mode of drying leaves

Removal of cadmium from aqueous solutions having various concentrations of cadmium using oven-dried leaves one time and naturally dried leaves another time was studied on five types of plant leaves. The results obtained are shown in Table 6. These results show little higher efficiency of naturally dried leaves ($\sim$ 18–20 °C) than

oven-dried leaves (70 °C). Applying the analysis of variance (ANOVA) statistical test on the results of Table 6 indicated a significant difference between the natural-dried and the oven-dried leaves. The obtained *p* values were 0.0012, 0.0003, 0.0003, 0.0008 and 0.0000 for styrax, plum, pomegranate, walnut and meddler plant leaves, respectively. This difference in the adsorption capacity might be due to the destruction of some of the adsorption sites of the oven-dried leaves because of the effect of temperature. The order of efficiency of naturally dried leaves also is different from that of the oven-dried leaves. The efficiency of removal of cadmium by naturally dried leaves is arranged in the decreasing order: plum > styrax > medlar > pomegranate > walnut leaves.

3.7. Effect of size of leaves

Removal of cadmium from aqueous solutions by five types of plant leaves was studied using three different sizes of each type of plant leaves. These three sizes were (i) normal untouched leaves, (ii) roughly crushed leaves and (iii) ground to 0.6–0.7 mm pore radius. The results obtained indicate a distinct dependence of the efficiency of removal of cadmium on the size of plant leaves. For all types of studied leaves and from all studied concentrations of cadmium, the efficiency of removal of cadmium by plant leaves can be arranged in the decreasing order:

Ground leaves > crushed leaves > untouched leaves.

This arrangement is expected because adsorption of cadmium on leaves is directly related to surface area. This surface area increases with crushing and with grounding leaves.

3.8. Effect of agitation

The effect of casual agitation of leaf suspensions on the efficiency of plant leaves to remove cadmium from aqueous solutions was studied using several types of plant leaves and several combinations of plant leaves. Examples of the results obtained are given in Table 7. A statistical test, ANOVA, was applied on the results of Table 7. This test

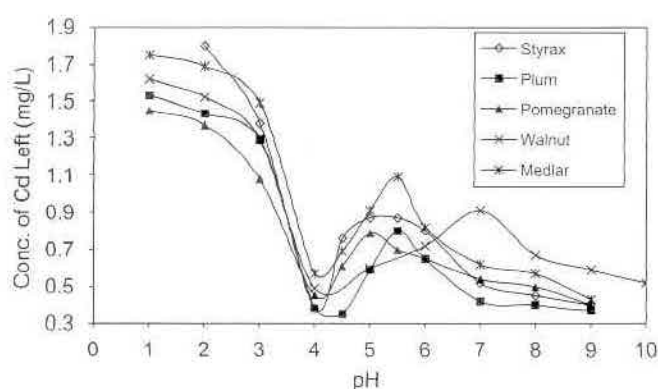


Fig. 2. Effect of pH on the removal of cadmium by several types of leaves. Concentration of Cd = 2.0 mg/l; concentration of leaves = 12.0 g/l.

Table 6
Effect of mode of drying leaves on their removal of cadmium from solution

Fraction of Cd removed										
Initial Cd conc. (mg/l)	Medlar		Walnut		Pomegranate		Plum		Styrax	
	Naturally dried	Oven dried	Naturally dried	Oven dried	Naturally dried	Oven dried	Naturally dried	Oven dried	Naturally dried	Oven dried
1.0	0.87	0.73	0.82	0.76	0.84	0.76	0.89	0.80	0.88	0.82
3.0	0.88	0.74	0.84	0.76	0.86	0.77	0.91	0.82	0.90	0.83
5.0	0.90	0.75	0.86	0.77	0.88	0.78	0.93	0.83	0.92	0.84
7.0	0.91	0.76	0.87	0.78	0.89	0.79	0.94	0.85	0.93	0.85
10.0	0.92	0.77	0.88	0.78	0.90	0.80	0.95	0.85	0.94	0.86

All readings are taken after equilibrium is attained (120 h for styrax, 96 h for walnut and 72 h for the remaining types of plant leaves). Concentration of leaves = 12.0 g/l; pH = 4.0.

showed a significant difference between the adsorption capacities of cadmium from agitated and non-agitated solutions. The obtained *p* values were 0.004, 0.004, 0.005 and 0.004 for styrax, plum, walnut and styrax–plum combined plant leaves, respectively.

The effect of agitation of solution is related to the rate-limiting step. This is discussed in Section 3.13.

3.9. Effect of presence of foreign ions and of complexing agents

The effect of the presence of various concentrations of zinc, lead and copper foreign ions and of the EDTA complexing agent on the efficiency of removal of cadmium by plant leaves was studied on five types of plant leaves.

Table 7
Effect of agitation of solution on the removal of cadmium by plant leaves

Time/h	Styrax		Plum	
	Without agitation	With agitation	Without agitation	With agitation
<i>Conc. of Cd adsorbed (mg/g)</i>				
1.5	0.27	0.31	0.25	0.32
5.0	0.35	0.38	0.30	0.35
10.0	0.39	0.44	0.39	0.43
24.0	0.46	0.49	0.48	0.51
48.0	0.52	0.54	0.60	0.66
72.0	—	—	0.71	0.72
96.0	0.69	0.71	—	—
120.0	0.72	0.72	—	—
Leaf type	Walnut		Styrax + Plum	
	Without agitation	With agitation	Without agitation	With agitation
<i>Conc. of Cd removed (mg/g)</i>				
1.5	0.25	0.33	0.23	0.29
5.0	0.34	0.37	0.29	0.34
10.0	0.37	0.41	0.35	0.39
24.0	0.48	0.50	0.46	0.49
48.0	0.55	0.56	0.54	0.57
96.0	0.65	0.67	0.71	0.72

Concentration of Cd = 10.0 mg/l; concentration of leaves = 12.0 g/l; pH = 4.0.

Table 8
Effect of presence of Cu^{2+} , Zn^{2+} , Pb^{2+} and EDTA in solution on the removal of cadmium using plant leaves

Plant leaves	Fraction of cadmium removed							
	Conc. of Zn (mg/l)		Conc. of Cu (mg/l)		Conc. of Pb (mg/l)		Conc. of EDTA (mg/l)	
	2.0	10.0	2.0	10.0	2.0	10.0	2.0	10.0
Styrax (1)	0.75	0.62	0.77	0.66	0.76	0.64	0.74	0.61
Plum (2)	0.71	0.58	0.76	0.63	0.76	0.64	0.72	0.58
Pomegranate (3)	0.70	0.57	0.70	0.55	0.72	0.61	0.77	0.53
Walnut (4)	0.66	0.51	0.69	0.56	0.70	0.60	0.62	0.51
1 + 2	0.73	0.59	0.75	0.64	0.76	0.64	0.73	0.60
2 + 4	0.69	0.56	0.70	0.58	0.70	0.62	0.65	0.53
1 + 2 + 3	0.70	0.56	0.72	0.62	0.72	0.63	0.68	0.55
1 + 2 + 3 + 4	0.72	0.57	0.73	0.53	0.73	0.64	0.70	0.57

Concentration of Cd = 2.0 mg/l; concentration of leaves = 12.0 g/l; pH = 4.0. All readings are taken after 120 h.

The results obtained are given in Table 8. These results indicate noticeable effects of the presence of all studied foreign ions and of EDTA on reducing the efficiency of plant leaves to remove cadmium from aqueous solutions. This effect increases with increasing the concentration of the present foreign ion or complexing agent. The effect of the studied chemicals on reducing the efficiency of removal of cadmium by plant leaves can be arranged in the order:



The effect of presence of foreign ions was found in some cases to reduce the efficiency of removal of metal ions by plant leaves. For example, the presence of lead and cadmium reduced the removal of copper by poplar leaves (Al-Subu et al., 2001); the presence of copper and cadmium reduced the removal of lead by cypress leaves (Salim et al., 1994); and the presence of copper reduced the removal of cadmium by beech leaves (Salim et al., 1992).

The presence of other ions enhanced the removal efficiency of metal ions by plant leaves. For example, the presence of zinc ions enhanced the removal of copper by poplar leaves (Al-Subu et al., 2001); the presence of magnesium and sodium ions enhanced the removal of lead by cypress leaves (Salim et al., 1994); and the presence of lead ions enhanced the removal of cadmium by beech leaves (Salim et al., 1992).

Wang (1995) concluded that the binding sites on the water hyacinth roots have higher affinity for lead compared to that of cadmium and zinc. Similar results were observed by Low et al. (1994).

All above studies indicate that the effect of presence of foreign ions on the removal capacity is complicated. This effect depends on several factors such as:

1. The competition on the adsorption sites between the foreign and the removed ions. This competition is influenced by the charge and size of the hydrated ions involved.
2. Some of the ions present are expected to make complexes with reagents leached from plant leaves into

solution. This affects the ability of these ions to compete for adsorption sites.

- Added ions affect the pH of solution to various degrees. This has great influence on the removal efficiency of metal ions.

The role of EDTA is to change the free cadmium ions into complex ions. The present results suggest that adsorption of complex cadmium ions on plant leaves is less than that of the free cadmium ions. This is probably due to the larger size of the complex ion compared to the free cadmium ion. The large size of the complex ion deprives it from a part of the adsorption sites that can be reached only by the small free cadmium ions.

3.10. Release of cadmium from charged plant leaves

Samples of 12 g/l styrax, plum, walnut and combined styrax–plum plant leaves were saturated with cadmium by soaking each of them in 10 mg/l aqueous cadmium solutions for a long time (1 week). This resulted in the transference of ~85% of cadmium from solution onto leaves. These leaves were then put in solutions having various concentrations of H^+ , Zn^{2+} , Cu^{2+} and EDTA, and the release of cadmium from leaves was followed with time. Two values of pH were used for this study, one is more acidic and the other is more basic than the optimum pH chosen for the removal of cadmium (c.f. Fig. 2).

The obtained results are shown in Figs. 3–5 for the release of cadmium under the effects of pH, competing ions and EDTA, respectively. These results indicate that:

- Cadmium is partially released from plant leaves under the effect of variation of pH, addition of competing ions or the addition of EDTA.
- About half of the cadmium in leaves is released during the first 1–5 h of the influence of the releasing agent.
- The release of cadmium from plant leaves is continued for a long time under the influence of the releasing agents. However, a part of cadmium in leaves resists being released after very long times of contact with the releasing agents. This is due to an equilibrium reached between the amount of cadmium released and that linked again to the bound sites. The unreleased part of

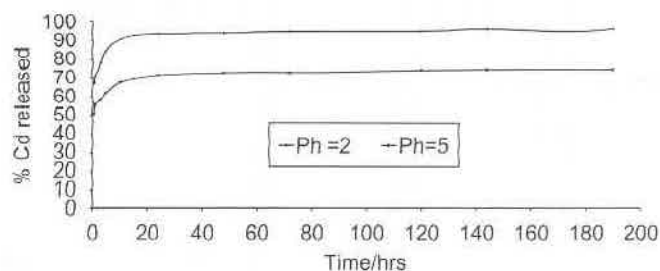


Fig. 3. Release of cadmium from charged styrax plant leaves by changing the pH of the solution.

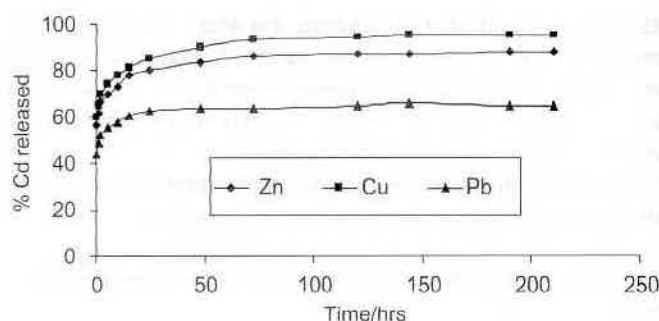


Fig. 4. Release of cadmium from charged styrax plant leaves by the addition of 10 mg/l competing ions at pH 4.0.

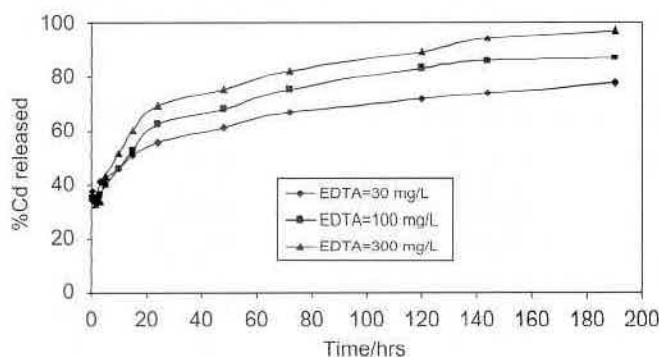


Fig. 5. Release of cadmium from charged styrax plant leaves by the addition of various concentrations of EDTA.

cadmium in leaves is ~20% under the influence of acidification, ~16–45% under the influence of addition of competing ions and ~15–34% under the influence of addition of increasing concentrations of EDTA.

- The effect of competing ions on the release of cadmium from plant leaves can be arranged in the decreasing order: copper > zinc > lead.

3.11. Application of adsorption isotherms

The Freundlich and the Langmuir adsorption isotherms are the most widely applied isotherms for the adsorption of metal ions on a wide variety of adsorbents.

The Freundlich isotherm is an empirical one appropriate for the adsorption processes where non-uniformity of the surface of adsorbent is expected. An appropriate formula of the Freundlich adsorption isotherm is:

$$\log C_s = \log K + 1/n \log C_l$$

where C_s is the concentration of metal ion adsorbed (mg/g), C_l the concentration of metal ion remaining in solution (mg/l), K the constant indicating the adsorption capacity of the adsorbent and n the constant indicating the adsorption intensity of the adsorbent.

The Langmuir adsorption isotherm is commonly applied to monolayer chemisorption of gases. However, several authors have applied this isotherm for the adsorption of metal ions on sorbents. This isotherm is mainly applied

when no strong adsorption is expected and when the adsorption surface is uniform. A commonly used formula of the Langmuir adsorption isotherm is

$$1/C_s = 1/b + 1/ab(1/C_i)$$

where C_s and C_i are as defined in the Freundlich isotherm, a is the constant indicative of the bonding energy between the adsorbent and the adsorbed species and b the constant indicative of the mass of the adsorbed species required for a monolayer coverage of a unit mass of adsorbent.

The applicability of the above isotherms on the present results was tested on a representative group of results of Table 4 containing plant leaves having high, medium and low efficiencies of removal of cadmium from aqueous solutions. Both the Freundlich and the Langmuir adsorption isotherms showed linear relationships on the present results (shown in Figs. 6 and 7 for the Freundlich and the Langmuir adsorption isotherms, respectively). The parameters of the Freundlich adsorption isotherm were calculated from the results of Fig. 6. The values of the parameter n are 1.09, 0.93, 0.87 and 0.78 for n values of styrax, walnut, olive, vine and lemon leaves, respectively. The values of the parameter K are 358.8, 166.4, 67.0, 41.7 and 25.9 for styrax, walnut, olive, vine and lemon leaves, respectively. The parameter n for all studied types of leaves

is ~ 1 , indicating low coverage of cadmium on leaves. The values of this parameter show also the decrease of the intensity of adsorption of cadmium with decreasing efficiency of removal of cadmium by plant leaves. The values of the parameter K also indicate decreasing capacity of adsorption of cadmium with decreasing efficiency of removal of cadmium by plant leaves. The values of the parameters n and K obtained in this work are close to the values obtained from previous works on the removal of cadmium by plant leaves (Sayrafi et al., 1996; Salim and Abu-El-Halawa, 2002; Salim et al., 1992).

The parameters of the Langmuir adsorption isotherm, a and b , were found to be erroneous and with negative values for most of the present results. This suggests the unsuitability of this isotherm for application on the present results. Such negative values of the Langmuir parameters were reported in a previous work on the removal of lead on pine leaves (Al-Subu, 2002). The negative values of the Langmuir parameters were attributed to the non-uniformity of plant-leaf surfaces and to the high strength of adsorption of lead on pine leaves (Al-Subu, 2002). These same reasons are probably the cause of the negative values of the Langmuir parameters found for the present results.

3.12. Order of reaction

For each initial concentration of cadmium, in the results presented in Fig. 1, the values of C_s were plotted against the square root of time $t^{1/2}$. These plots gave straight lines (examples of the obtained lines are shown in Fig. 8). The slopes of these lines were used to obtain the rates of reaction:

$$(dC_s/dt) = 1/2t^{1/2}(dC_s/dt^{1/2}).$$

The obtained rates of reaction were found to be linearly related to C_i (examples of the obtained lines are shown in Fig. 9). This indicates a first-order reaction, with respect to cadmium, for the process of the removal of cadmium on plant leaves. This conclusion was tested and found true for several types of leaves and leaf combinations. The tested

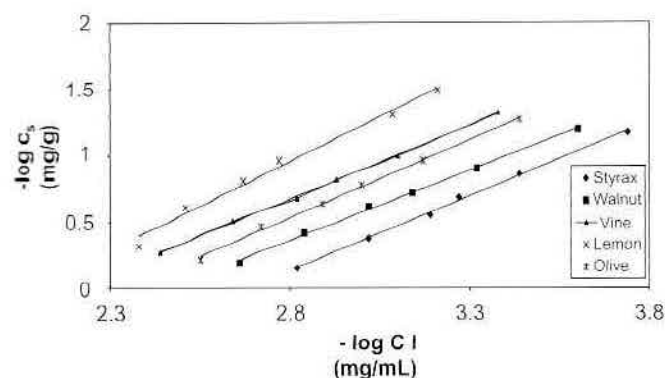


Fig. 6. Linear relations of adsorption of cadmium on plant leaves according to the Freundlich adsorption isotherm.

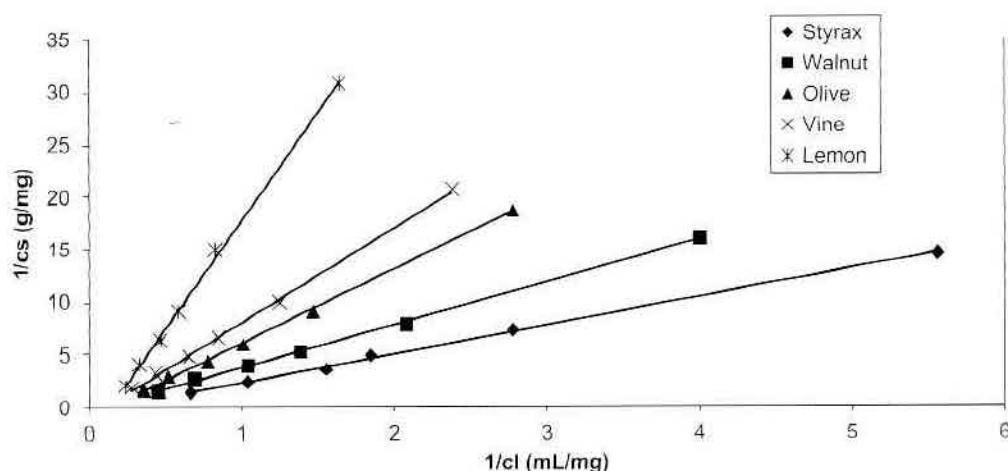


Fig. 7. Linear relations of adsorption of cadmium on plant leaves according to the Langmuir adsorption isotherm.

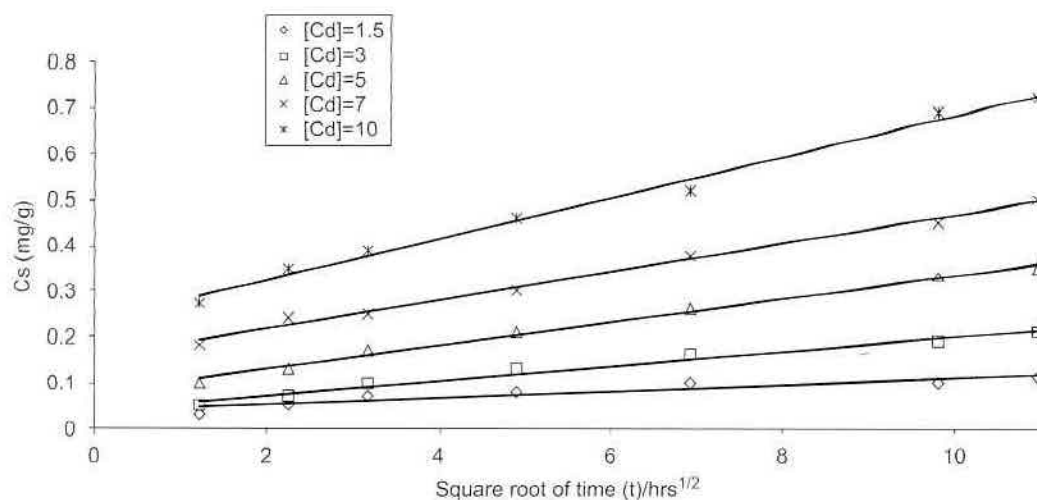


Fig. 8. Relations of C_s and $t^{1/2}$ for the removal of cadmium from aqueous solutions having various concentrations of cadmium.

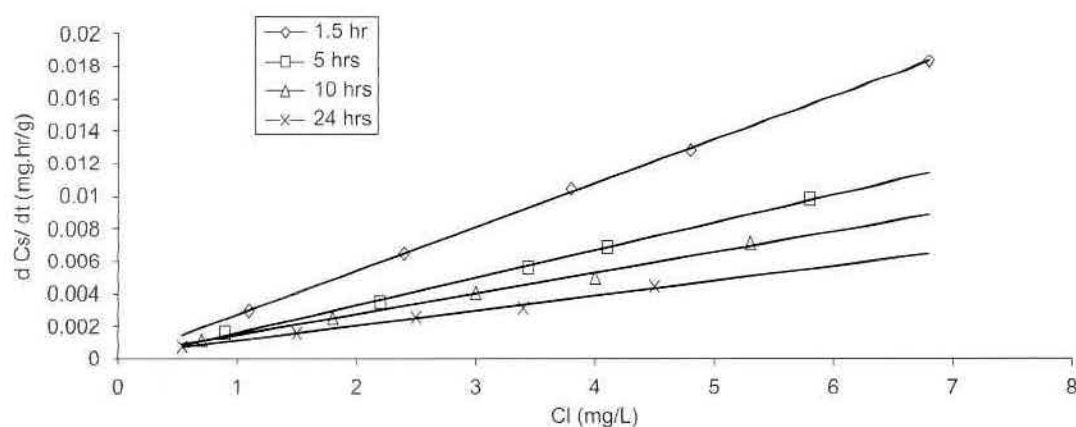


Fig. 9. Relations between the rate of removal of cadmium on styrax plant leaves from solutions having various concentrations of cadmium and after several times of contact between solutions and plant leaves.

leaves were styrax, plum and walnut plant leaves. The tested combinations of plant leaves (in equal weight ratios) were styrax + plum, styrax + walnut, plum + walnut, and styrax + plum + walnut leaves.

3.13. Rate-limiting step

Adsorption of metal ions on plant leaves follows a three-step process (Salim et al., 1992):

1. Film diffusion: in which metal ions reach by diffusion, driven by a concentration gradient, the surface of leaves.
2. Intra-pore diffusion: in which most of the adsorbed metal ions have to enter the pores of the leaves in order to reach the internal adsorption sites.
3. Adsorption: in which the metal ions become adsorbed on the adsorption sites.

The straight-line relations found between C_s and $t^{1/2}$ (c.f. Fig. 8) suggests that diffusion is the rate-limiting step (Helfferich, 1962; Weber et al., 1963). The small effect of

agitation (c.f. Table 7) suggests that intra-pore diffusion is the rate-limiting step for the removal of cadmium by plant leaves. The same conclusion was also suggested for the uptake of cadmium on beech leaves (Salim et al., 1992).

4. Conclusions

Plant leaves are capable of removing cadmium from aqueous solutions. The efficiency of removal varies widely from one type of plant leaves to another. The efficiencies of removal of cadmium by the studied species can be arranged in the decreasing order:

Activated carbon > styrax > plum > pomegranate > walnut > medlar > cypress > mulberry > carob > olive > eucalyptus > pistachio > almond > vine > fig > apricot > oak > pine > apple > orange > lemon leaves.

All combinations of styrax with other types of plant leaves result in additive effects on the efficiency of removal of cadmium; all other combinations of plant leaves result in antagonistic effects on the efficiency of removal of cadmium.

The maximum removal efficiency of cadmium by plant leaves is not affected by cadmium concentration in aqueous solutions. However, the range of concentration studied in this work is not wide. It is probable that by using a wide range of initial cadmium concentrations, the differences in sorption capacity would be more appreciable. The pH of solution affects highly the removal efficiency of cadmium; the maximum efficiency is obtained at pH 4.1. The efficiency of removal of cadmium increases with the increase in the concentration of plant leaves used for the removal of cadmium from aqueous solutions. The naturally dried plant leaves are more efficient than oven-dried leaves for removing cadmium from solution. Ground plant leaves have higher efficiency than untouched or roughly crushed leaves for removing cadmium from aqueous solutions. Agitation of solution increased slightly the efficiency of removal of cadmium by plant leaves.

The presence of foreign ions and of the complexing agent, EDTA, reduced the efficiency of removal of cadmium by plant leaves. The effect of the studied chemicals on reducing the efficiency of removal of cadmium can be arranged in the decreasing order: EDTA > Zn^{2+} > Pb^{2+} > Cu^{2+} .

Cadmium ions can be released from plant leaves, charged with cadmium, by changing the pH of solution, by the addition of a competing ion or by the addition of EDTA. However, a part of the cadmium adsorbed by plant leaves resists being released by all used releasing agents.

The present results of removal of cadmium by plant leaves and by combined plant leaves follow the Freundlich adsorption isotherm. Parameters of this isotherm indicate the variations in the adsorption capacity and adsorption intensity of cadmium on the studied plant leaves according to their various efficiencies of removal. The results give straight lines according to the Langmuir adsorption isotherm. However, the parameters obtained from the present results, according to this isotherm, are negative and meaningless.

The results of the present work suggest a first-order reaction, with respect to cadmium, for the removal process of cadmium by plant leaves. There are indications that the rate-limiting step for the removal process is intra-pore diffusion.

The method presented in this work might be of interest for industrial and for environmental applications for the removal of toxic metal ions from the environment. Using plant leaves for the removal of metal ions have the advantages of being available, cheap and efficient. The contaminated plant leaves are expected to precipitate and become a part of the sediment. However, using this method for treatment of industrial effluents might require finding a way for a proper disposal of the leaves.

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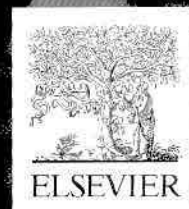
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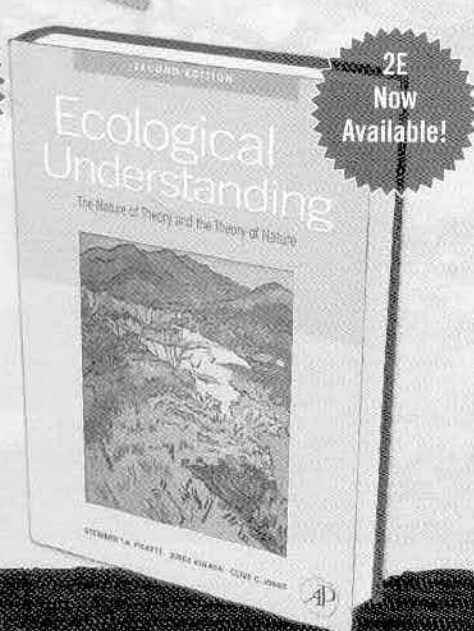
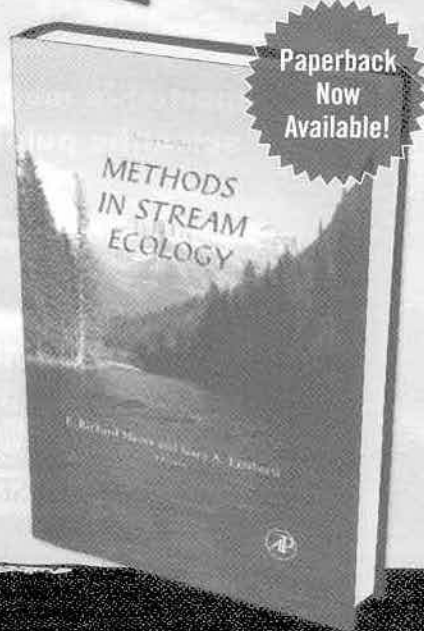
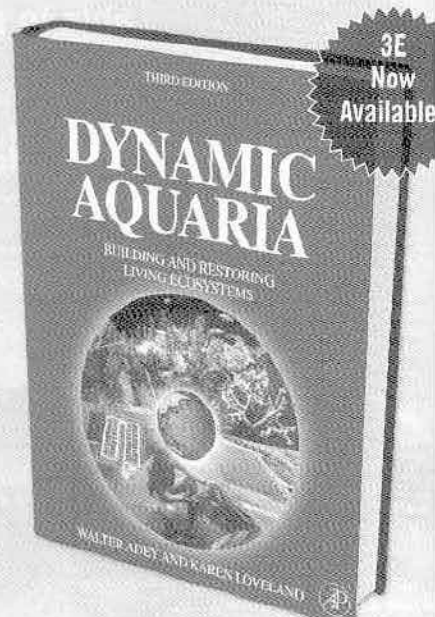
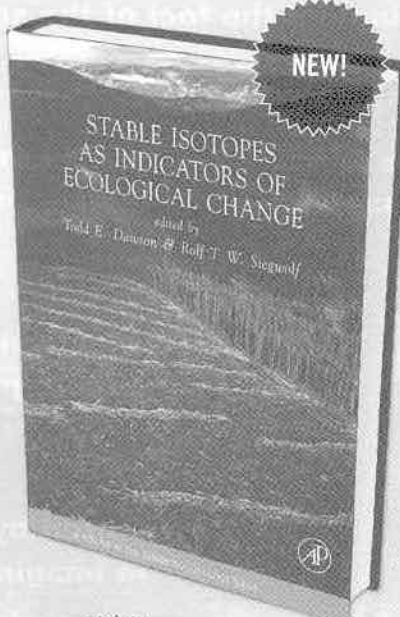
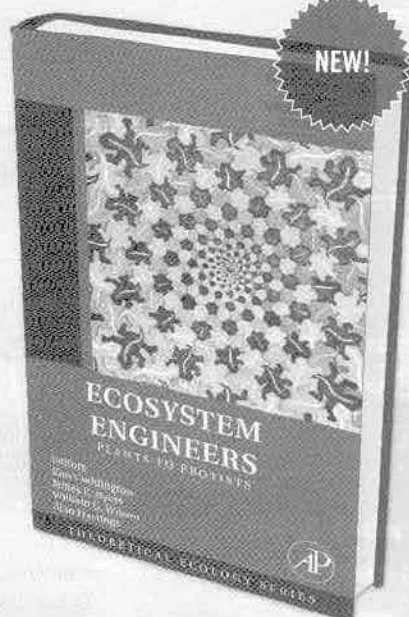
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