Solid Waste: Assessment, Monitoring and Remediation
Twardowska, Allen, Kettrup and Lacy (Editors)

III.4
Sewage sludge

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III.4.1. Introduction

Sewage sludge is a by-product of wastewater treatment at sewage treatment works. Effluents are received from industrial, municipal or rural sources. The sewage sludge is derived from primary, secondary and tertiary treatment processes (ANDERSEN-SEDE, 2001). In the Working Document on Sludge 3rd Draft (EC DG ENV, 2000), it is proposed to use the definition of sludge suggested by CEN (European Committee for Standardization): "mixture of water and solids separated from various types of water as a result of natural or artificial processes". *Sewage sludge* would then be "sludge from urban wastewater treatment plants". The suggested definition of *treated sludge* is that of "sludge, which has undergone one of the treatment processes…or a combination of these processes, so as to significantly reduce its biodegradability and its potential to cause nuisance as well as the health and environmental hazards when it is used in land". Sewage sludge belongs to the large group of *biodegradable waste (biowaste)* that means "any waste that is capable of undergoing anaerobic digestion or aerobic decomposition" (EC DG ENV, 2001).

Managing municipal and industrial waste presents a major challenge for today's society. Current approaches to waste management tend to focus on avoidance of waste generation and reutilization of waste products without adversely affecting the environment, rather than waste disposal, wherever feasible (EC DG ENV, 1999, 2001). Due to the progressive implementation of the Urban Waste Water Treatment Directive 91/271/EEC (EEC, 1991) in all EU Member States, and rise in the number of households connected to sewers, the annual generation of sewage sludge is constantly growing. The increase of the level of sewage treatment also adds to the amount of sewage sludge produced. In 1995–1998, in 5 of 14 EU Member States (Sweden, Denmark, Finland, The Netherlands and Germany) the percentile of population covered with the upgraded sewage treatment with biogen removal exceeded 70% (EUROSTAT, 2001). In other countries the level of sewage treatment is continuously increasing. Due to the combined effect of these factors, the annual generation of sewage sludge in the European Community is heading from some 5.5 Mt (million tons) in 1992, through 7 Mt in 1997 towards about 9 Mt by the end of 2005 (ANDERSEN-SEDE, 2001; Langenkamp et al., 2001a; EC, 2002). The current sludge production in 12 EU Member States (without Greece, Spain and Italy) ranges from 16 to 35 kg/person/a; in Greece it accounts for 9 kg/person/a (Langenkamp et al., 2001a). The increasing trend of sewage sludge generation has been observed all over the world that prioritizes the issue of its environmentally sound and sustainable management. Sludge is rich in organic matter and nutrients such as nitrogen, phosphorus and potassium, and thus is an attractive material to be used in agriculture as a fertilizer or a soil improver. However, due to the original pollutant load of the treated sewage and processes involved in sewage treatment, sludge tends to concentrate heavy metals, organic contaminants and pathogenic organisms. The presence of toxic heavy metals and organic compounds, excess phosphorus and nitrogen, in addition to hygienic concerns, presents a challenge to wastewater treatment facilities in selecting appropriate technology and means of recycling or disposal of sludge, both from an economical and environmentally acceptable perspective (Harris-Pierce et al., 1995). Effects from these constituents may be immediate, or time delayed and non-linear (Van den Berg, 1993).

The primary objective of sludge management in the European Community is to utilize the opportunity of its beneficial use in agriculture. Simultaneously, the new regulations under development are focused on long-term protection of Community soils, to assure safety to human health and to the environment in view of the most recent scientific and technological progress. A focus on these objectives has resulted in a number of comprehensive state-of-the art review studies commissioned by the European Commission in several research centers, which on one hand, evaluate occurrence of contaminants in sewage sludge, potential risk from its use in agriculture and treatments for reduction of harmful substances and pathogens (ANDERSEN-SEDE, 2001; Carrington, 2001; ICON, 2001; Langenkamp et al., 2001a), and on the other hand, analyze background trace element and organic matter content of European soils and define short- and long-term actions for setting up a European Soil Monitoring System (Balze et al., 1999; Langenkamp et al., 2001b). Other feasible and environmentally friendly ways of sewage sludge utilization are also considered.

The evaluation of sludge quality presented here is largely based on these sources. On its background, the approach to the limit values of trace elements in soil and sewage sludge used in agriculture will be discussed, along with other options of this waste utilization.

III.4.2. Sludge quality

III.4.2.1. Occurrence and sources of pollutants

The physical separation, biological and chemical treatment of wastewater produce sewage sludge. Screenings, grit, scum, septic material, filter backwash and other wastewater solids are all found in sludge. They provide additional solids to the sludge from primary, secondary and tertiary treatment processes. The chemical composition of municipal sewage sludge can vary greatly, depending on the composition of wastewater, and applied wastewater and sludge treatment processes. As sewage sludge sequesters hydrophobic compounds, concentrations of pollutants in this material reflect the flow of chemicals in a contemporary society (Hale et al., 2002). Sources of pollutants in urban wastewater (UWW) that become subsequently enriched in sewage sludge are shown in Figure III.4.1.

Before disposal or recycling, sludge is subject to undergo one or several treatment processes such as thickening, dewatering, stabilization, disinfection and thermal drying, in

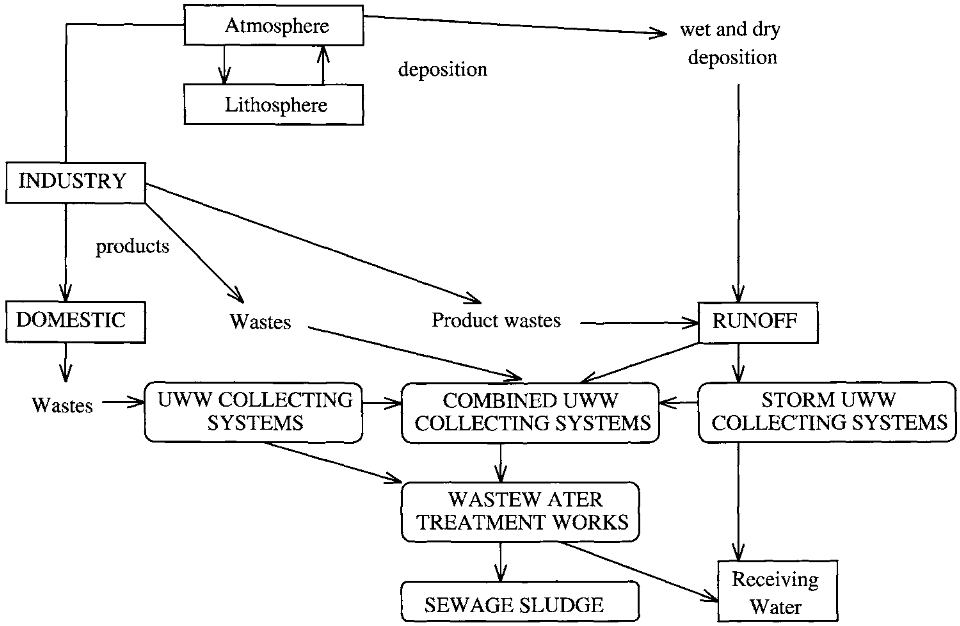


Figure III.4.1. Source of pollutants in urban wastewater and sewage sludge (ICON, 2001, modified).

order to reduce water content, biodegradability and improve hygienic properties. Apart from the enrichment of above-mentioned constituents of agricultural value (organic matter, nitrogen, phosphorus, potassium, and to a lesser extent, calcium, magnesium and sulfur), sewage sludge is significantly enriched in organic pollutants, trace metals and pathogens. The EC study performed by ICON (2001) formulates the type and loads of both organic and metal pollutants in wastewater (sewage) treatment systems and consequently in sewage sludge as a complex function of:

- size and type of conurbation (commercial, residential, mixed);
- plumbing and heating systems;
- domestic and commercial product formulation and use patterns;
- dietary sources and feces;
- atmospheric quality, deposition and run-off;
- presence and type of industrial activities;
- use of metals, and other materials in construction;
- urban land use;
- traffic type and density;
- urban street cleaning;
- maintenance practices, for collecting systems and stormwater control;
- accidental releases.

The pollutants that through the wastewater treatment process accumulate in sewage sludge, thus posing a potential risk to the environment, represent three major groups:

- potentially toxic elements (PTEs) that include heavy metals: Cd, Cr(III) and Cr(VI), Cu, Hg, Ni, Pb, Zn, Ag, platinum group metals (PGMs) and metalloids (As, Se);
- organic pollutants;
- pathogens.

III.4.2.2. Heavy metals

The heavy metal content in sewage sludge has been of major concern for many years. Heavy metals in UWW (sewage) tend to be associated with suspended solids and are partitioned into the sludge during treatment. Conventional sewage treatment removes 60–72% of cadmium (Cd), 28–73% of chromium (Cr), 45–70% of copper (Cu), 20–70% of nickel (Ni), 54–73% of lead (Pb) and 40–74% of the zinc (Zn) from the influent and consequently enriches sewage sludge with these metals. A wide range of metal concentrations may be present in sludge, due to differences in sewage metal concentrations. Contents that exceed common values indicate substantial contamination from industrial sources (Weber et al., 1984; Wong et al., 2001). An EC report prepared by ICON (2001) differentiates three major sources of PTEs entering the wastewater (sewage) treatment plant and sewage sludge as the target recipient: (1) domestic, (2) commercial/industrial and (3) urban run-off (Table III.4.1). The degree of uncertainty in the estimation of proportion of the particular sources in the metal load accounts for $\geq$50% of the total inputs of Cr, Ni and Zn, 20–40% of Cu, Hg and Pb and $<$20% of Cd.

Commercial/industrial inputs are estimated to be the major sources of Hg, Cr and Cd, and are considered to be responsible for up to 60% of these metals enrichment in wastewater and sewage sludge. Identified domestic sources contribute particularly significantly to the loads of Pb, Cu, Zn and Ni (up to 50–80%), while up to 20–40% of the total load of Cd, Pb, Zn is supplied with run-off (mass balance of Zn, Ni and Cr has been incomplete due to difficulties in identifying and evaluating part of the sources). The share of these sources in the total load may vary in a broad range, depending on the structure and significance of the industry. In some areas, the proportion of non-point metal input may be dominating, e.g. in the primary industrial areas of historically high long-term emission.

Table III.4.1. Estimated load of potentially toxic elements (PTEs) from different sources entering urban wastewater (UWW) system in the EU countries (% of the total input) (after ICON, 2001).

Heavy metals (PTE)	Sources (% of total input)		
	Domestic	Commercial/industrial	Urban run-off
Cd	20–40	30–60	3–40
Cr	2–20	35–60	2–20
Cu	30–75	3–20	4–6
Hg	4–5	50–60	1–5
Ni	10–50	30	10–20
Pb	30–80	2–20	30
Zn	30–50	5–35	10–20

The provisional metal source balance presented in Table III.4.1 is valid for the EU area, but may substantially differ from other areas with diverse economy, climatic conditions and urban infrastructure.

Limit values for metal content in sewage sludge from wastewater treatment plants have been set in the EU Sludge Directive 86/278/EEC (1986). A more stringent new draft regulation has been proposed by EC DG ENV, 2000. These regulations define sewage sludge and soil quality for the protection of soil when sludge is applied to agricultural land. The reported contemporary metal content in the sewage sludge from wastewater treatment plants (WWTPs) in the EU Member States vary in a broad range, generally within an order of magnitude (Table III.4.2). These metal contents appear to be well below the limit values.

The EU reports (ANDERSEN-SEDE, 2001; ICON, 2001) point out the general declining trend in metal concentrations in wastewater and sewage sludge in the EU Member States over the past two decades (up to 10% for Ni, 40–50% for Cr, Hg and Pb, and up to 60% for Cd), which is attributed mainly to efficient trade effluent controls, optimization of technological processes and overall structural changes in industrial production.

Data on sewage sludge quality in the EU Accession countries and available data for some other countries (e.g. Israel) show that concentrations of the most heavy metals fall within the range reported for the EU and all the data, including the priority hazardous substances Cd and Hg, are below the limit values set by the EU regulations in force and as a draft. Average content of Hg is within or only slightly above (Czech Republic) that in the EU, while Cd appears to be more problematic, and in Latvia, Slovenia and Poland its

Table III.4.2. Range and average metal content in sewage sludge vs. limit values in the EU (in mg/kg d.m.) (after ICON, 2001; ANDERSEN-SEDE, 2001).

Heavy metal	Concentrations in sludge		EU limit values for sludge		EU limit values for soil	
	Mean[a]	Range[b]	86/278/EEC	EC DG ENV (2000)[c]	86/278/EEC	EC DG ENV (2000)[c]
Cd	2.2 (2.8)[d]	0.4–3.8	20–40	10	1–3	0.5–1.5
Cr	79 (141)[e]	16–275		1000		30–100
Cu	337	39–641	1000–1750	1000	50–140	20–100
Hg	2.2	0.3–3	16–25	10	1–1.5	0.1–1.0
Ni	37	9–90	300–400	300	30–75	15–70
Pb	124	13–221	750–1200	750	50–300	70–100
Zn	863 (1222)[f]	142–2000	2500–4000	2500	150–300	60–200

[a]Arithmetic mean from data reported for 13 countries: Austria, Denmark, Finland, France, Germany, Greece (Athens), Ireland, Luxembourg, Norway, Poland, Sweden, The Netherlands and UK.
[b]EU Member States only.
[c]The Working Document on Sludge, 3rd Draft (2000).
[d]Data without parenthesis exclude Poland: the mean Cd content in Polish sludge is 9.9 mg/kg d.m.
[e]Data without parenthesis exclude Greece: the mean Cr content in sludge from Athens is 886 mg/kg d.m.
[f]Data without parenthesis exclude Poland and Greece (Athens): the mean Zn content in Polish sludge is 3641 mg/kg d.m., in Greece (Athens) 2752 mg/kg d.m.

average concentrations in sludge about twofold exceed the EU range: in Latvia and Slovenia these values are above 7 mg/kg d.m. (ANDERSEN-SEDE, 2001) in Poland 9.9 mg/kg d.m. (ICON, 2001), in Israel (one plant) 10.7 mg/kg d.m. (Avnimelech and Twardowska, 1997).

The PTEs listed above that include Cd, Cr(III) and Cr(VI), Cu, Hg, Ni, Pb, Zn, Ag and metalloids (As, Se) are considered to be the priority inorganic pollutants in the EU, the USA and Canada. Their contents in biosolids and soil are regulated and extensively tested, while other metals detected in sewage sludge that may be potentially harmful to risk receptors such as soil biota and grazing animals are not well quantified and evaluated with respect to safe application in agriculture. Hargreaves and Hale (2002) suggest quantifying in biosolids a number of other unregulated metals, such as Al, Ag, Ba, Be, Bi, Mo, Fl, Sb, Sr, Th, Ti and V.

Recently, due to the significant expanding of the commercial use of the PGMs that includes Pt, Pd, Rh, Ru, Ir and Os, mainly in vehicle exhaust catalysts for reduction of atmospheric emissions of CO, hydrocarbons and NO_x from internal combustion engines, and in minor amount (6–12%) in anti-neoplastic drugs used in hospitals for cancer treatment, these metals have appeared in municipal wastewaters. Approximately 70% of Pt is transferred to the sewage sludge. Reported concentrations of Pt in sludge from two WWTPs in Munich (Germany) were in the range 86–266 μg/kg d.m. (ICON, 2001).

Rose and Swanson (2002) report also the concentration of medical radioisotopes (I-125, Ir-192, Sm-145 and Cs-137 with half-lives of 60 days, 74 days, 320 days and 30 years, respectively) in sewage sludge exemplified in three WWTPs in the New York area. According to these authors, the potential of posing a threat to human health from such sludge transformed to biosolids for land application may occur, as these isotopes have half-lives longer than the time of sludge digestion process.

III.4.2.2.1. Source control

Analysis of status and further development of source control of PTEs in the European community was carried out for EC Directorate General – Environment by ICON (2001).

For efficient source control, identification and quantification of sources of PTEs, and the development of a complete mass balance from each source are required. In the EU up to now, though, for a high proportion of major PTEs, sources are not yet identified and there is a substantial uncertainty in the mass balance, the highest for Cr, Ni and Zn ($\geq 50\%$), lower for Cu, Hg and Pb (20–40%) and the lowest for Cd ($< 20\%$). Despite these uncertainties, efforts to reduce metal discharges to sewer systems resulted in significant decrease of metal contents in the sewage sludge. Effective implementation of effluent controls, technology optimization and change in industrial structure in the EU Member States have also contributed to the decrease in metal content in sewage sludge. ICON (2001) reports reduction of input concentrations of Cd to WWTPs in the UK and Sweden during 1992–1998 by 60%, Cr, Hg and Pb by 40–50%, Zn and Ni by 10% and no change in Cu inputs that reflects the share of industrial sources in these countries in the total input load.

Besides large industrial installations that are subject to rigorous waste control standards, discharge of metals plays significant role in small commercial, artisan enterprises such as vehicle workshops and washing facilities, metal processing and goldsmiths, and also health establishments and hotels/catering, which are also supposed to comprise a major proportion of the incomplete information and unidentified inputs of metals to UWW systems (Table III.4.1). Metal loads discharge to sewer systems from small business enterprises is more difficult to control. Compulsory wastewater pretreatment before discharge and inspections of the premises may markedly reduce the input of metals from artisan activities to the sewer system and to the sewage sludge. As has been shown in case studies (ICON, 2001), reduction of Zn, Cu and Pb may reach up to < 10%, Cr and Ni up to 0.5% and Cd up to 40% of the total metal load entering WWTP.

Reduction of metals from domestic sources and run-off is particularly problematic and feasibility of its control is limited. According to ICON (2001), the principal sources of metals in domestic wastewater are body care and cleaning products, pharmaceuticals, liquid wastes (e.g. paints) and plumbing (Cu and Pb source). The referred report sees a way of reducing these metal inputs in a participation of homeowners in voluntary collection schemes for liquid waste. It, though, seems that the only practicable way of efficient reduction of metal inputs from households is the minimization of metal contents in the household products by manufacturers.

III.4.2.3. Organic pollutants

III.4.2.3.1. Occurrence and sources

The studies of ICON (2001) and Langenkamp et al. (2001a) for the EC reviewed about 150 literature sources published in the last decade, in addition to older literature reviews that cover a period since late 1970s. Data on the occurrence of organic pollutants in sewage sludge were collected and discussed with respect to basic toxicological issues, transfer pathways and risk assessment. In both referred EC review studies (ICON, 2001; Langenkamp et al., 2001a), a limited number of available data on organic pollutants in sewage sludge (generally, within the range from < 10 to several tenths of samples for each of 3–4 countries) is evident. This reflects the lack of routine testing due to analytical difficulties and costs, and lack of standardized methods of analysis, as well as the lack of an agreement on the kind and number of specific substances to be tested in a group of chemicals (e.g. data for PAHs comprise from 8 to 18 compounds, for PCBs 6–7 congeners) that limits the comparability of data.

Sewage sludge was found to carry the highest load of organic contaminants among fertilizers. Organic micropollutants, or xenobiotics, are widespread in the environment as a result of human activities such as industry, agriculture and traffic (Berset and Holzer, 1995). They are persistent in nature and concerns exist regarding their toxicity and the tendency for some of them to bioaccumulate through the food chain (Jones et al., 1995). Through the UWW systems they enter the wastewater treatment facilities and finally sewage sludge; the residue level of organic pollutants increases from raw to digested sludge. Organics found in sewage sludge include, but are not limited to, adsorbable organic halogen compounds (AOX), polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Seven PCDDs, 10 PCDFs and 12 PCBs are jointly referred to as dioxin-like compounds; this term is currently in a wide use (e.g. WHO, 1999; Larsen et al., 2000; US EPA, 2000a; Van den Berg et al., 2000). According to ICON (2001), due to introduction of source and emission controls on persistent organic contaminants in the 1980s, significant reduction of industrial inputs of these compounds to sewers (up to >90 to >99%) and consequently decrease of their concentrations in sewage sludge in the EU Member States occurred. The current contents of persistent organic contaminants in this waste result mainly from:

- background inputs to the sewer from normal dietary sources;
- background inputs by atmospheric deposition due to contemporary remobilization/volatilization from soil and cycling in the environment (PCB, PCDD/F, PAH);
- atmospheric deposition from waste incineration (PCDD/F);
- atmospheric deposition from domestic combustion of coal;
- the limited biodegradation of organic contaminants during sludge treatment;
- the increase of the concentration of these compounds in sludge due to volatile solids destruction during sludge treatment.

In countries, where controls on industrial combustion and incineration emissions are unsatisfactory, these processes, along with small consumers (household and trade activities) and the production of chlorinated pesticides are the principal sources of persistent organic contaminants (PAH, PCB, PCCD/F) in sludge.

Other widespread organic contaminants in sewage sludge originate from their domestic and commercial use and comprise detergent residues, nonylphenol and nonylphenol ethoxylates with one or two ethoxy groups (NPE), surfactants – linear alkylbenzene sulfonate (LAS), and di-2-(ethylhexyl)phthalate (DEHP) used in plastic manufacture. Many other emerging organic compounds identified in sludge create problems due to their persistence in soil or during sewage or sludge treatment, or toxic effects, e.g. organotins (such as mono-, di- and tributylin MBT, DBT and TBT) (Langenkamp et al., 2001a); commercial chlorinated paraffin (a large group >200 formulations) used as plasticizers in plastics, extreme pressure additives, flame retardants, sealants and paints; brominated diphenyl ethers (PBDE), increasingly used as flame retardants in furnishing, textiles and electrical insulation; polychlorinated naphthalenes (PCNs) originated from waste incineration or landfilling of items containing PCN; quintozene (pentachloronitroenzene); nonvolatile silicone polymers polydimethylsiloxalanes (PDMSs) used in lubricants, electrical insulators and antifoams; nitro musks (chloronitrobenzenes) that are components of perfumed cosmetic products; endogenous estrogens (17β-estradiol and estrone) and synthetic steroids that are ingredients of oral contraceptives; pharmaceutical compounds used in medical and veterinary practice; or polyelectrolytes based on polyacrylamide and cationic copolymers and used for sludge treatment as dewatering aid (ICON, 2001). The list of organic pollutants occurring in sewage sludges reflects current trends in their production and use. A comprehensive literature review by Drescher-Kaden et al. (1992) concerning organic pollutant residues with proven or suspected toxic effects detected in German sewage sludge in 1977–1992, cited in both recent EC review sources (ICON, 2001; Langenkamp et al., 2001a), refers to 332 compounds, of that 42 of them were present regularly, mostly in the range from mg/kg to g/kg d.m.

Concentration range and mean contents of major groups of organic contaminants in sewage sludge from different European countries in 1989–1996 collected in the review studies accomplished for the EC by ICON (2001) and Langenkamp et al. (2001a) are presented in Table III.4.3.

Table III.4.3. Occurrence of selected organic contaminants in sewage sludge in 1989–1996 vs. limit values (MCL) proposed by EC DG ENV (2000) (after ICON, 2001; Langenkamp et al., 2001a).

Organic compounds	Country (sludge treatment)[a] [number of samples/ WWTPs tested]	Years[b]	Concentrations (mg/kg d.m.)[c]			MCL[d]
			Mean[e]	Range		
Halogenated organics (AOX)	Denmark [NA]	1995	200	NA	75–890	500
	Germany [NA]	1994–1996		196–206	NA	
Linear alkylbenzene sulfonates (LAS)	Denmark (V) [26, *19*]	1993–1995		455–530	11–16,100	
	Germany (And) [*8*]	NA, –2000		NA	1600–11,800	
	Germany (Ae) [*10*]	As above		NA	182–452	
	Italy (And) [*1*]	1996–1997		NA	11,500–14,000	
	Norway [36]	NA, –2000	6500	54	<1–424	2600
	Spain (And) [*3*]	As above		NA	12,100–17,800	
	Spain (Raw) [*2*]	As above		NA	400–700	
	Switzerland (And) [*10*]	As above		NA	2900–11,900	
	UK (And) [*5*]	As above		NA	9300–18,800	
D(2-ehylhexylphtalate) (DEHP)	Denmark [29]	1993–1995		24.5–38	3.9–170	
	Norway [55]	1989 +	20–60	58–83	<1–1115	100
	Sweden [27]	1989–1991		170	25–661	
Nonylphenol and ethoxylates (NPE)	Denmark [29]	1993–1995		NA–8	0.3–537	
	Norway [55]	1989 + [b]	26	136–189	22–2298	50
	Sweden [60]	1989–1993		82–825	23–7214	
	UK [NA]	NA		330–640	NA	
Polycyclic aromatic hydrocarbons, total (PAH)	Denmark 18 PAH [29]	1993–1995		NA	<0.01–8.5	
	Germany 6 PAH [124]	NA, –2000		NA	0.4–12.83	
	Germany 16 PAH [88]	As above	0.5–27.8	NA	0.25–16.28	6[f]
	Norway [36]	NA, –2000		3.9	0.7–30	

(*continued*)

Table III.4.3. (Continued)

Organic compounds	Country (sludge treatment)[a] [number of samples/ WWTPs tested]	Years[b]	Concentrations (mg/kg d.m.)[c]			MCL[d]
			Mean[e]		Range	
	Sweden 6 PAH [NA]	NA, –1997		1.6	NA	
Polychlorinated biphenyls, total (PCB)	Germany 6 PCB [NA]	1989–1996	0.09	0.154–0.34	NA	0.8[g]
	Norway 7 PCB [36]	NA, –2000		0.0422	0.017–0.10	
	Sweden 7 PCB [27]	1989–1993		0.113–0.1	0.0006–7	
	USA [NA]	–1998		NA	0.21 (98.P)	
Polychlorinated dibenzo-dioxins and -furans (PCDD/F) (ng TEQ/kg d.m.)	Austria [NA]	NA, –1999	36	14.5	8–38	100
	Denmark [9]	1993–1994		NA	10.3–34.2	
	Denmark [NA]	NA, –1999		21	0.7–55	
	Germany [NA]	As above		20–40	0.7–1207	
	Germany [NA]	1994–1996		17–22	46–56 (90.P)	
	Spain [NA]	NA, –1999		64	NA	
	Sweden [14]	1989–1991		20.5 (50.P)	5.7–115	
	Sweden [NA]	NA, –1999		20	0.02–115	
	Sweden [36]	NA, –2000		6.26 (50.P)	3.0–68.8	
	UK [NA]	NA, –1999		NA	9–192	
Organotins						
MBT	Switzerland [*4*]	1988–1990	NA	NA	0.10–0.97	NA
DBT	Switzerland [*4*]	1988–1990		NA	0.41–1.24	
TBT	Switzerland [*4*]	1988–1990		NA	0.28–1.51	

[a]Sludge treatment: (V), various; (And), anaerobically digested; (Ae), aerobic process; (Raw), non-treated.
[b]–2000, data before 2000; 1989+, data after 1989.
[c]Concentrations in mg/kg d.m., except for PCDD/F, given in ng TEQ/kg d.m.
[d]Proposed EU 2000 (3rd draft) limit concentrations in sewage sludge used in agriculture (EC DG ENV.E.3/LM, 2000).
[e]Mean concentration values: left column – for the several EU countries (after ICON, 2001); right column – for each specific country.
[f]Sum of 11 compounds: acenaphtene, phehahthrene, fluorine, fluoranthene, pyrene, benzo(b + j + k)fluoranthne, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-c,d)pyrene.
[g]Sum of six congeners PCB 28, 52, 101, 138, 153, 180; WWTP, wastewater treatment plant; NA, not available; 50.P and 98.P, 50 and 98 percentile of a compound concentration, respectively.

The highest enrichment in sewage sludge shows the surfactants LAS and nonylphenol NPE that also significantly exceed the proposed EU concentration limits for sludge to be used in agriculture. The data for LAS prove that these compounds are not completely degraded during mesophilic anaerobic digestion, which is the principal commonly used sludge stabilization process, thus their high accumulation in the anaerobically digested sludge. The LAS concentration range in aerobically digested or untreated sludge appeared to be visibly narrower.

The broad concentration range and variations in toxic organics content are also of concern, in particular that the variations observed within one waste treatment plant can be greater than the differences in concentration range between different plants (Langenkamp et al., 2001a). High maximal concentrations and broad concentration range are characteristic also for DEHP. PAHs in some reported cases exceed the rigorous proposed EU limits, both with respect to mean and maximal contents.

Source and emission control on combustion and incineration emissions and production of certain chlorinated pesticides, as well as the ban on use of PCB resulted in efficient reduction of persistent compounds such as PAH, PCB and PCDD/Fs in the primary industrial/commercial sources, up to >90 to $>99\%$, and consequently caused an adequate decline of input to sewage sludge from these sources. The contemporary principal inputs of these contaminants to the environment, and also to sewage sludge, have shifted to much less controllable sources such as small consumers including households and surface run-off or remobilization/volatilization of background (historical) contaminant loads from soil (ICON, 2001). Also long-lived applications of industrial chemicals such as PCBs (e.g. electrical equipment) may emit them to the environment during use and disposal for a long time (Breivick and Alcock, 2002; Breivick et al., 2002). Generally, the reported actual concentrations of PCDD/Fs and PCBs in sewage sludge in the EU countries appear to be safely below the precautionary limits proposed by the EC.DG.ENV.E3/LM, 2000 (3rd draft). Nevertheless, due to the aforementioned environmental cycling of these chemicals, their occurrence in wastewater and in sewage sludge cannot be neglected.

High concentrations of PAHs in sewage sludge are particularly problematic; flue gases from traffic account for one of the major sources of PAH release to the environment. Measurements of 16 PAHs content in dust particulates suspended in the ambient air in the vicinity of gasoline stations, car parks, bus terminals and along the roads, conducted in 2000 in the thickly populated industrial Silesia Land, Poland, showed high and variable concentrations of these compounds, many times exceeding standards and off-road background contents (Table III.4.4). Therefore, this source can contribute significantly to the elevated contents of PAHs in the sewage sludge.

Besides AOX, LAS, NPE, DEHP, PAH, PCB, PCDD/F and TBT that are considered as priority organic pollutants and thus received relatively much, but still not enough attention, there is a limited data on the environmental behavior, fate and risk associated with a number of organic compounds occurring and accumulating in sewage sludge during waste treatment process, e.g. with hormone steroids, both natural, as estrone (E1), 17β-estradiol (E2) and estriol (E3), and synthetic, as 17α-ethynylestradiol (EE2) and mestranol (MeEE2) that belong to a group of endocrine disruptors. Estrogenic steroids were reported to occur in influents to sewage treatment plants in different countries (UK, Italy, Canada, Brazil, Denmark, Japan, Germany) in concentrations

Table III.4.4. Mean concentrations of selected PAHs in the ambient air in the vicinity of gasoline stations, car parks, bus terminals and along the roads in 2000 in Silesia Land, Poland (after Klejnowski et al., 2002).

Statistical parameter	Concentration (ng/m^3)											
	BaA		BbF + BkF		BaP		CHR		INP + DbahA		$\sum$16 PAH	
	S	W	S	W	S	W	S	W	S	W	S	W
Mean	49.5	36.2	19.3	74.6	88.2	116.2	96.8	98.9	76.0	87.2	1427	1558
Minimum	0	0	0	0	0	0.5	0	0	0	0	568.0	643.5
Maximum	376.8	209.9	398.0	398.2	463.9	407.3	604.8	320.9	228.8	396.5	3609	2240
Standard deviation	63.6	46.8	63.3	114.7	83.9	107.0	105.5	72.1	40.9	75.6	467.6	359.6

BaA, benz(a)anthracene; BbF + BkF, benzo(b)fluoranthene + benzo(k)fluoranthene; BaP, benzo(a)pyrene; CHR, chrysene; INP + DbahA, indeno(1,2,3-cd)pyrene + dibenz(a,h)anthracene; $\sum$16 PAH, sum of 16 PAHs; S, summer; W, winter.

ranging from < 1 up to several tenths ng/l. Their removal rate during sewage treatment, partially due to adsorption on sludges was found to be high and for different estrogens and treatment plants varied within the range from 61 to >99%, thus their considerable enrichment in sewage sludge can be anticipated (Ying et al., 2002a). In the sludge dry matter from German WWTPs, several estrogenic endocrine disruptors, 17α-ethinylestradiol (EE2), 4-*tert*-octylphenol (OP), 4-nonylphenol (NP) and bisphenol A (BPA) were found in significant concentrations: up to 280, 13.3, 560 and 32 mg/kg d.m., respectively (Gehring et al., 2003). Studies on occurrence of about 100 of human and veterinary pharmaceuticals in the influents and effluents from WWTPs showed decrease from μg/l to ng/l range during the treatment process that suggests their adequate enrichment in sewage sludge. The fate of these compounds in wastewater and sewage treatment process is not well understood (Schrap et al., 2003).

Other authors (Cloup et al., 2003) report frequent occurrence of biocides at ppb level in sewage sludge from 12 WWTPs, of these permethrin and tributylin contents were the highest with a mean 98 and 148 ppb d.m., respectively. Water run-off was considered as the main source of permethrin, diuron and carbendazin, and the industry as a complementary source of diuron. Biocides are widely applied as disinfectants for public/private areas and in veterinary hygiene, as wood/masonry preservatives and conservators in non-alimentary finished products.

While PCBs, due to past restrictions on their use and improved industrial source control decline as chemicals of concern, unrestricted and unregulated polybrominated diphenyl ethers (PBDEs), among them penta-BDE mixture that serves as flame retardant additive in polymers used, e.g. in polyurethane foam for furniture, thermoplastics for electronics and in textile back coatings, have become environmentally problematic. In North America that consumes over half of the world's production of PBDEs and 98% of penta-BDE, these compounds have been detected in all compartments of the environment, in animals and humans, exhibiting persistence and bioaccumulative properties similar to PCBs. PBDE concentrations appeared to be also the highest in North American sewage sludges (typically over 1 mg/kg), while content levels elsewhere (in the EU, UK, Australia, New Zealand and Hong Kong) were much lower. One of the sources of PBDE enrichment in sewage sludge is considered to be urban dust (Hale et al., 2002).

Besides xenobiotic organic compounds of different kinds that enter to the sewage sludge through wastewater, there is also a purposeful introduction of such substances in the sludge treatment process. Polyelectrolytes based on polyacrylamide and cationic copolymers are used extensively in this process to aid the mechanical dewatering process. This results in high concentration of these compounds in sludge, in the range 2500–5000 mg/kg. Acrylamide is a common monomer associated with polyelectrolytes. They are reported to be potentially toxic to humans and have a carcinogenic effect. This caused their withdrawal from use in Japan and Sweden and restrictions in Germany and France. In many other countries polyelectrolytes in sludge treatment are used unrestrictedly (ICON, 2001).

These examples show that sewage sludge is a sink for many organic compounds. Their persistence in the environment, the exposure and possible effects on the environment and human health are not yet thoroughly understood.

III.4.2.3.2. Source control

The EC review study prepared by ICON (2001) summarizes the relative importance of contemporary sources of the major groups of organic contaminants in sewage sludge, as well as reduction opportunities for these compounds (Table III.4.5).

The major problematic organic compounds of high relevance to the industrial/commercial and domestic sources comprise detergent surfactants and residues (LAS and NPE), DEHP that originates from the production and use of finished products from PVC, such as floor and wall plastic coverings and textile prints, and pharmaceuticals. The source control of these compounds at the producer side is considered possible mainly through limitation of LAS surfactants and NPE use by substituting them in detergent formulations and DEHP in plastic manufacture. At the consumer side, the use of these chemicals is planned to be reduced through eco-labeling and extensive information about advantages and disadvantages of currently used chemicals and their prospective substitutes. Human and veterinary pharmaceuticals occurrence in the sewage sludge can be partially limited through the collection system for unwanted drugs, as well as through segregation and pre-treatment of hospital, medical center and laboratory effluents. Financial incentives for encouraging municipalities and household owners to remove lead piping in the areas with soft water and to remove old lead paints have also been recommended.

Due to aforementioned efficient control of PAHs and PCDD/F emission from the industrial sources, and a ban on PCB use, surface run-off becomes the major source of these compounds in wastewaters and consequently in sewage sludge. This source is generally difficult to control. A substantial reduction of PAH emission to the environment from traffic sources can be achieved through rigorous technical control of exhaust gases in

Table III.4.5. Major sources and possibility of control of organic contaminants entering urban wastewater and sewage sludge in the EU Member States (after ICON, 2001).

Organic contaminant[a]	Manufacturing/ commercial		Run-off		Domestic	
	Relative importance	Opportunity to reduce	Relative importance	Opportunity to reduce	Relative importance	Opportunity to reduce
LAS	H	M	L	L	H	M
NPE	H	M	L	L	H	L
DEHP	H	M	L	L	M	M
PAH	L	L	H	L	L	L
PCB	L	L	H	L	L	L
PCDD/F	L	L	H	L	L	L
Pharmaceutical	H	M	L	L	H	M

H, high; M, moderate; L, low.
[a]LAS, linear alkylbenzene sulfonates; NPE, nonylphenolethoxylates; DEHP, di(2-ethylhexyl)phtalate; PAH, polycyclic aromatic hydrocarbons; PCB, polychlorinated biphenyls; PCDD/F, polychlorinated dibenzo-*p*-dioxins and dibenzo-*p*-furans.

cars and other motor vehicles and withdrawal of old vehicle fleets not adequately equipped to meet the requirements.

Development of the sustainable urban drainage with individually assessed and implemented low- and high-tech solutions has been considered as effective method of pollutant input from the run-off source, along with increasing control on emissions to water, air and land, and a close monitoring and control for connection of small users, hospitals, dental and medical practices, garages and car washes to the UWW systems.

III.4.2.4. Pathogens

The report by Carrington (2001) for the EC DG ENV (EC Directorate General – Environment) points out the variability of the quantity and species of pathogens with time and location depending upon local circumstances and the current population health (Table III.4.6).

These data show that for safe use of sewage sludge on the agricultural land, a reduction of at least 10^4 of added *Salmonella* and the destruction of viability of *Ascaris* ova is required, which means that the level of pathogen content in sewage sludge should not exceed the ambient levels in the environment. This level of hygienization is demonstrated by WWTPs, which treat sewage sludge by advanced processes listed in Table III.4.7. Conventional treatment processes do not sufficiently reduce the risk of pathogen transmission and thus must be restricted with respect to sludge applied to land.

Monitoring of treated sludge for the presence of pathogens is considered impracticable. For evaluation of sludge quality, use of surrogate organisms such as *Escherichia coli* and *Clostridium perfringens* commonly found in sludge that have similar resistance to treatment as pathogens is suggested. The recommended numbers of *E. coli* in treated sludge should be ≤ 1000 per gram (d.m.), and of *C. perfringens* ≤ 3000 per gram (d.m.).

Hygienic requirements are considered in the EU both by the regulations in force (EEC, 1986) and in the Working document on sludge (EC DG ENV, 2000). According to this document, the advanced sludge treatment process shall be initially validated through a 10^6 reduction of a test organism such as *Salmonella senftenberg* W 775. The treated sludge shall not contain *Salmonella* sp. in 50 g (wet weight) and

Table III.4.6. Typical concentrations of microorganisms (wet weight) in untreated sewage sludge (after Carrington, 2001).

Microorganisms	Species	Concentration range (cells/g)
Bacteria	*E. coli*	10^6
	Salmonella	10^2-10^3
Viruses	Entero-	10^2-10^4
Protozoa	*Giardia*	10^2-10^3
Helmints	*Ascaris*	10^2-10^3
	Toxacara	$10-10^2$
	Taenia	5

Table III.4.7. Advanced hygienization treatments of sewage sludge (after Carrington, 2001).

Process	Parameters
Windrow composting	Batches of sludge (± bulking agent) to be kept at 55°C for 4 h between each of three turnings, followed by a maturation period to complete the composting process
Aerated pile and invessel composting	The batch to be kept at a minimum of 40°C for at least 5 days and for 4 h during this period at a minimum of 55°C. This to be followed by a maturation period to complete the composting process
Thermal drying	The sludge should be heated to at least 80°C for 10 min and moisture content reduced to < 10%
Thermophilic digestion (aerobic or anaerobic)	Sludge should achieve a temperature of at least 55°C for a minimum period of 4 h after the last feed and before the next withdrawal. Plant should be designed to operate at a temperature of at least 55°C with a mean retention period sufficient to stabilize the sludge
Heat treatment followed by digestion	Minimum of 30 min at 70°C followed immediately by mesophilic anaerobic digestion at 35°C with a mean retention time of 12 days
Treatment with lime (CaO)	The sludge and lime should be thoroughly mixed to achieve a pH value of at least 12 and a minimum temperature of 55°C for 2 h after mixing

the treatment shall achieve at least a 10^6 reduction in *E. coli* to less than 5×10^2 CFU/g.

For biowaste that is a much broader group of organogenic waste and comprises also sewage sludge, in the EC Working document on biowaste, 2nd draft (EC DG ENV, 2001), as test organism for the hygienic requirements, *Salmonella streptococchi* and *C. perfringens* have been selected. Biowaste is deemed to be sanitized if *S. streptococchi* is absent in 50 g of compost/digestate and *C. perfringens* is absent in 1 g of compost/digestate. Both documents are widely discussed and the final decisions concerning hygienization criteria are to be approved.

The US federal rules (US EPA, 1993) pertaining to pathogens in land-applied sewage sludge are technology based and no risk assessment was performed. A study commissioned by the US EPA and by the National Research Council of the National Academy of Sciences and released in 2002 (NRC, 2002) found that there is uncertainty about the potential for adverse human health effects from exposure to biosolids and recommended a new survey of pathogens in sludges, reassurement of risks based on more recent methodology including pathogens, and development of improved pathogen detection methods and indicator organisms (Hanlon, 2002; Harrison and McKone, 2002).

III.4.3. Sludge treatment technologies and management

III.4.3.1. Sludge treatment technologies

The problem of sludge management is neither simple nor cheap. Increasingly stringent regulations and new technologies to meet quality demands, e.g. progressive implementation of the Urban Waste Water Treatment Directive 91/271/EEC (1991) in all Member States of the EU, have resulted in the production of greater sludge quantities and types. Solids processing and disposal account for a significant proportion of the costs associated with the operation and maintenance of a WWTP. Hence, cost-effective, environmentally sustainable options must be sought.

Before utilization or disposal, sludge has to undergo one or several treatment processes aimed to reduce its water content and fermentability, and to hygienization. The steps of sludge treatment are presented in Table III.4.8.

Sludge processing methods generally should consider the following:

- sources, quantities and characteristics of the wastewater;
- best available treatment technologies;
- regulatory, public health and environmental considerations;
- performance and costs.

A comprehensive short description of existing sewage sludge treatment processes can be found in the EC study (ANDERSEN-SEDE, 2001). The details of treatment technologies are widely presented in the relevant technical literature and guideline sources are not addressed in this chapter, and only their environmental aspects are discussed here.

Table III.4.8. Sludge treatment processes (after ANDERSEN-SEDE, 2001).

Steps	Types of processes	Objectives
Conditioning	Chemical conditioning Thermal conditioning	Sludge structure modification Improvement of further treatment
Thickening	Gravity thickening Gravity belt thickener Dissolved air flotation	Obtain sufficient density, strength and solids content to permit hauling for further disposal process Reduce the water content of the sludge
Dewatering	Drying beds Centrifuging Filter belt Filter press	Reduce the water content of the sludge
Stabilization and/or disinfection	Biological processes: *Anaerobic digestion* *Aerobic digestion* *Long-term liquid storage* *Composting* Chemical processes: *Lime treatment* *Nitrite treatment* Physical processes: *Thermal drying* *Pasteurization*	Reduce the odor generation Reduce the pathogen content of the sludge
Thermal drying	Direct Indirect	Highly reduce the water content

III.4.3.2. Effect of wastewater and sludge treatment on contaminants content and transformations

III.4.3.2.1. Heavy metals

Heavy metals enrichment in sludge depends on their content in influent to WWTP and efficiency of treatment processes. Metal transfer to sludge occurs during primary and secondary sedimentation as physico-chemical processes of gravitational separation of mineral particulate matter and microbial biomass, and metal uptake by flocks of microbial biomass during biological treatment step. Process of metal transfer from wastewater to sewage sludge is well described by existing empirical and mechanistic models. In general, 60–80% of most metals are transferred to the sludge except Ni that is removed in a lesser proportion (~40%) due to high solubility (ICON, 2001).

The wastewater treatment process determines metal content in sewage sludge, as practically no changes of metal load occur during sewage treatment, except of a minor loss of soluble metals during thickening and dewatering with removed water. In contrast, metal concentration in sludge increases proportionally to the decrease of its volume due to dewatering, but decreases after chemical treatment processes proportionally to the chemicals added.

III.4.3.2.2. Organic contaminants

Organic contaminants show much higher propensity to transformations during physical, chemical and microbiological treatment of the sludge that results in their loss, decomposition or formation of new compounds. The mechanisms of these processes include (ICON, 2001):

- volatilization;
- biological degradation;
- abiotic/chemical degradation, e.g. hydrolysis;
- extraction with excess liquors;
- sorption onto solid surfaces and association with fats and oils.

Many organics in wastewater are lipophilic and readily sorbed onto sewage sludge. Hydrophobic organic contaminants on wastewater have different affinity to sorption onto sludge solids during primary sedimentation process. Sorption potential and therefore enrichment in sewage sludge of individual compounds can be estimated by the octanol–water partition coefficient (K_{ow}) as low for log $K_{ow} < 2.5$, medium for $2.5 < K_{ow} < 4.0$ and high for log $K_{ow} > 4.0$.

Considerable part of volatile organics of high volatilization potential (Henry's law constant Hc $> 10^{-3}$ l/mol m^9), e.g. benzene, toluene, dichlorobenzenes in the wastewater and in sewage sludge may be lost in aeration/agitation process during wastewater treatment, and during thickening and dewatering when transferred to sludge.

Sewage treatment was estimated to biodegrade during the activated sludge process about 80% of LAS and of the endocrine disruptor 4-nonylphenol polyethoxylate (NP_nEO), although 97–99% degradation was also reported. About 15–20% of LAS accumulates in the raw sewage sludge. Microbial degradation of NP_nEO causes formation of relatively lipophilic metabolites NP_1EO and NP_2EO that also enrich the raw sewage sludge (ICON, 2001). Studies have found that alkylphenol ethoxylate (APE) metabolites are more toxic than the parent substances and possess the ability to mimic natural hormones by interacting with an estrogen receptor (Ying et al., 2002b). The alkylphenols 4-nonylphenol and 4-*tert*-octylphenol are known to be formed under anaerobic conditions, probably from long chain anionic tensides. In digested sludge a distinct increase of the concentration of bisphenol A, a monomer of polycarbonates and epoxy resins, have also been noted recently (Tennhardt et al., 2003).

Mesophilic anaerobic digestion may cause destruction of about 20% of the residual surfactants, and transformation of approximately 50% of NP_nEO metabolites into NP. Destruction efficiency may be enhanced by increasing digestion temperature and retention time (ICON, 2001). Nonetheless, there is strong evidence that although APEs are highly treatable in conventional biological treatment facilities, anaerobic conditions retardate biotransformation of APE metabolites and enhance their persistence (Marcomini et al., 1989; John et al., 2000; Ying et al., 2002b).

The potential to biodegrade during anaerobic digestion was found to relate to the size of alkyl side chains. Lower molecular weight phthalate esters and butyl benzyl phthalate are completely degraded in 7 days of anaerobic digestion at 35°C and thus are removable by the conventional process of anaerobic digestion. Compounds with larger C-8 groups such as di-*n*-octyl and DEHP are much more resistant to anaerobic microbial degradation (ICON, 2001).

Aerobic thermophilic treatment appeared to degrade APEs and their metabolites much faster than in anaerobic conditions (Banat et al., 2000; Ying et al., 2002b). Also phthalate esters (DEHP) are rapidly destroyed under aerobic conditions, thus their >90% reduction occurs in 24 h already during wastewater treatment in the activated sludge process. Under aerobic psychrophilic conditions, a high concentration decrease rate was observed for several estrogenic phenolic xenobiotics and natural and synthetic steroids (Tennhardt et al., 2003).

Thermophilic aerobic digestion process of stabilization during composting has the potential to biodegrade relatively persistent organic compounds in sludge. It has been reported that composting and sludge storage for 3 months provide similar reduction for organic compounds as does mesophilic anaerobic digestion. A relatively new enhanced treatment process of thermal hydrolysis conditioning prior to conventional anaerobic stabilization is supposed to enhance the efficiency of removal of organic contaminants from sludge, though the effects of this process are to be yet investigated (ICON, 2001).

Some surfactants, e.g. fluorinated compounds are known as resistant to biodegradation, and also to heat, acids, bases and oxidizing/reducing agents and thus are of high environmental concern. Recent studies on biodegradability of non-ionic and anionic fluorinated surfactants during aerobic and anaerobic treatment in 80 WWTPs proved that fluorinated alkylethoxylates, perfluorinated alkylsulfates and carboxylates biodegraded with formation of metabolites, while methyl ethers of fluorinated alkylethoxylates appeared to be resistant either to anaerobic or aerobic biodegradation (Schröder and Meesters, 2003). Though perfluorinated alkyl acids (PFAs) in wastewater and sludge were found to be not the sole source of these compounds entering the environment (Tolls and Sinnige, 2003), their proven high potential for persistence, bioaccumulation and toxicity (accumulative risk for children and adults greater than 10) (Purdy, 2003; Windle et al., 2003) suggest the need of better insight into the potential hazard and control of PFAs from different sources, including sewage sludge.

A number of other compounds that have propensity to partition onto sludge particulates show different biodegradability during the wastewater/sewage treatment process; data regarding the fate, behavior, degradability and toxicity of some of them are sparse and yet need to be investigated. The activity of endogenous estrogens and synthetic steroids is reported to be reduced by 90% during wastewater treatment; only <3% has been transferred into sewage sludge (ICON, 2001). The data on removal rates of different estrogens (E3, E2, EE2 and E1) during treatment in different WWTPs show though a broader range of efficiency, from 61 to 99.9%, and seasonally even from 7 to >99%. The reason behind this large difference is unclear. There are suggestions that activated sludge treatment process can consistently remove over 85%

of E2, E3 and EE2, but the removal performance of estrone (E1) appears to be less and more variable (Ying et al., 2002a).

Pharmaceutical compounds are often lipophilic and potentially bioaccumulative. A wide range of removal rates (7–96%, mean > 60%) of these substances during wastewater treatment has been reported. Many commonly used pharmaceuticals are soluble and/or readily biodegradable, though for many of them predicting fate and partitioning during wastewater treatment is not possible due to lack of data. The information on the fate and behavior in the treatment process of the large number (>200) of commercial chlorinated paraffins and nitro musks is also sparse, similarly as for the brominated diphenyl ethers (PBDEs) and PCNs of high toxic activity. Polymethylsiloxanes (PDMSs) were found to exhibit high persistency, though no bioaccumulation or significant environmental toxic effect has been observed. Polyelectrolytes based on polyactylamide used extensively in sludge treatment to aid dewatering and thus showing high enrichment in treated sewage sludge are reported to be carcinogenic (ICON, 2001). Knowledge about TBTO organotins presence and fate in sewage sludge is not yet satisfying (Langenkamp et al., 2001a).

Extensive studies on the biodegradation and transformations of a large group of emerging compounds during wastewater/sludge treatment are required to evaluate the significance of their release to the environment from these processes.

III.4.3.3. Waste utilization and disposal

Three main options for bulk management of treated sludge are considered at present, with different preference (e.g. Figure III.4.2): use in agriculture, incineration and landfilling. There are also other minor sewage sludge recycling routes that are close either to

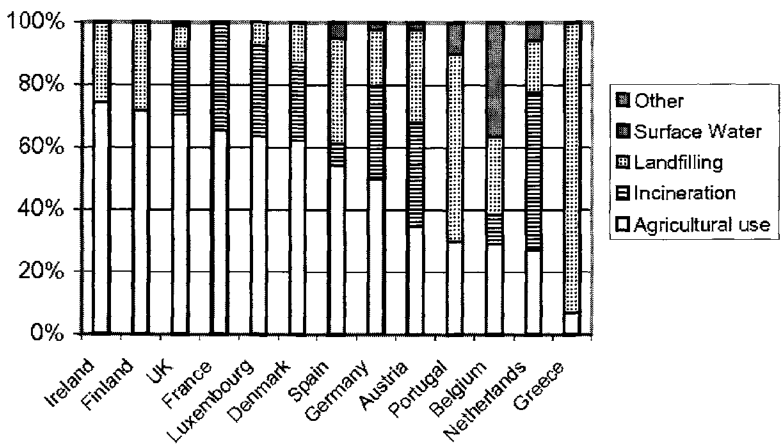


Figure III.4.2. Forecast of sludge utilization in the EU Member States by the year 2005 (after ANDERSEN-SEDE, 2001).

agricultural use (forestry and silviculture, land reclamation and revegetation) or presenting alternative solutions to combustion processes.

III.4.4. Use of sewage sludge in agriculture

III.4.4.1. General approach

The dramatic increase of sewage sludge generation in the EU that is estimated to reach nearly 9 Mt by the end of 2005 (Balze et al., 1999; ANDERSEN-SEDE, 2001; EC, 2002) brings about the increasingly difficult issue of its optimum disposal to all the acceptable outlets. The EU, through the existing Sewage Sludge Directive 86/278/EEC (EEC, 1986) being currently under revision that resulted in the development of Working documents on sludge (EC DG ENV, 2000) and biowaste (EC DG ENV, 2001) seeks ways to encourage the use of sewage sludge in agriculture and to regulate its use in such a way as to prevent harmful effects in soil, vegetation, animals and humans (EC, 2002). This is demonstrated in the increasing stringency of regulations concerning sewage sludge and soil quality, and in commissioning a number of feasibility studies on trace elements and organic matter contents in sewage sludge and European soils. Currently, at Community level the reuse of sludge in agriculture accounts for about 40% (EC, 2002). By 2005, forecasted agricultural use of sewage sludge in the EU should reach about 55% of the overall sludge generation. In Ireland, Finland, UK, France, Luxembourg, Denmark and Spain it will comprise over 60% of total. Predicted incineration rate will reach 23% and landfilling about 19% of total (Fig. III.4.2) (ANDERSEN-SEDE, 2001). Thus, agricultural use is going to be the dominant disposal outlet in the EU Member States.

In the USA, more than half of the 6.4 Mt of treated sewage sludges known also as biosolids are used as soil amendment (Harrison and McKone, 2002); agricultural use of biosolids shows increasing trend (Goldstein, 2000; Hanlon, 2002; NRC, 2002).

Another means of disposing sewage sludge in a way similar to agricultural use is its utilization in forestry, silviculture and green areas, and in degraded land reclamation.

III.4.4.2. Application of sewage sludge and soil protection

Soils are recognized as a finite, increasingly scarce and non-renewable resource. Their varying biological, chemical and physical properties should be protected and preserved in order to maintain ecological multifunctionality of soils. The protection of soils is and should be a principal objective of environmental policy that has been particularly stressed in the report by the European Soil Bureau to the EU-DG.ENV (Balze et al., 1999).

It is generally agreed that application of sewage sludge as a soil conditioner and fertilizer may supply plant needs for nutrients like nitrogen, phosphorus and organic matter, all necessary for plant growth and reproductive success. On the other hand, contamination of sewage sludge with pollutants often causes a low acceptance of this material. Among these pollutants, the presence of significant amounts of metals in sewage sludge is well established, which causes concern that long-term application of sewage sludge (biosolids) may contaminate soil, edible crops and groundwater (Balze et al., 1999; Wang et al., 2001).

III.4.4.3. Heavy metals in soils

III.4.4.3.1. Background contents

Soil contamination with heavy metals is a result of several processes including atmospheric pollution, the use of contaminated water for irrigation, phosphate containing fertilizers, and other materials used in farming, such as sewage sludge and composts applied as fertilizer. Sludge exhibits larger heavy metal concentrations than soils. This is of particular interest when the sludge is applied to land as a soil amendment. The natural heavy metal content of soils depends on the parent material from which they were derived by alteration processes (soil formation). Highly variable proportions of heavy metals such as Zn, Cd, Cu, Cr, Pb, Ni, etc. occur naturally in most soils (Kabata-Pendias, 2001) that need to be considered when evaluating the potential impact of metals on soils. Table III.4.9 provides some data on the background concentrations of metals found in soils in different countries.

Detailed knowledge of the background concentrations of heavy metals in soil, resulting mainly from geogenic factors, is indispensable for a reliable evaluation of soils in relation to the environmentally safe waste disposal options. Trace elements in soils have been a subject of research for decades. Extensive studies on the background levels of trace elements have been carried out in the different parts of the world (e.g. Kabata-Pendias, 2001; Yamasaki et al., 2001). Nevertheless, knowledge on the background levels of metals in soils, also in most European countries, at the beginning of the new Millennium appeared to be inadequate or scarce, despite existence of the Soil Profile Analytical database within the European Soil Database. Besides, there were problems with linking available metal concentrations data to the geographical soil map and with compilation of data from different countries and sources, which resulted from different understanding of the term "background levels" and variations in sampling and analytical methods. Data were also scarce on the spatial deposition of metals through land application or management of sewage sludge.

This situation was the basis for commissioning by the EC DG.ENV to the European Soil Bureau (ESB) a study on trace element and organic matter content of European soils. Within this study, the available information was elicited, the needs for standardization ascertained, the major gaps in data being filled and a harmonized European Soil Monitoring System set up using as a basis existing soil monitoring systems in the European countries (Balze et al., 1999; Langenkamp et al., 2001b, 2003). The mapping of trace elements in soils and establishment of a Geochemical Baseline for Europe is in a final stage. At this stage, the establishment of a common framework through the harmonization, introduction of standard methods and integration of the concept of bioavailability into the regulatory system become crucial. A novel idea for soil protection in Europe is a development of the EU Soil Thematic Strategy linked with a possible systematic approach provided by the European Integrated Environment and Health Monitoring System (Bidoglio, 2003). The build up of a Global Integrated Environment and Health System would have been a target for the next decades of this Millennium.

Table III.4.9. Natural background concentrations of metals in agricultural soils (after Kabata-Pendias, 2001).

Countries	Soil	Cd		Cr		Cu		Hg		Ni		Pb		Zn		As		Mo		Se	
		From to	Mean	From to	Mean	From to	Mean	From to	Mean	From to	Mean	From to	Mean	From to	Mean	From to	Mean	From to	Mean	From to	Mean
Australia	Sand			1.4–3.5									57	39–86				2.6–3.7			
	Loess			13–30	16																
	Clay				24																
Canada	Sand	0.10–1.8	0.43	2.6–34.0				0.01–0.7	0.06			2.5–47.5	10			1.1–28.9	5.8	0.4–2.5	1.5	0.1–0.32	0.27
	Loess	0.12–1.6	0.64													1.3–16.7	4.8				
	Clay							0.02–0.78	0.13	3–98	23	1.5–50	16.5	15–20				0.93–4.7	1.7	0.13–1.67	0.43
	Different															<1–30	5.8				
Japan	Sand															1.2–6.8	4.0				
	Different			3.5–810	50	5–176	34	0.08–0.49	0.28		28	5–189	35			0.4–70	11	0.2–11.3	2.6		
France	Different							0.03–0.5	0.4												
Germany	Sand													40–76							
	Loess					14–31								58–100							
	Clay					16–70								40–50						0.8–0.3	0.3
	Different			9–57	28			0.025–0.35	0.09		19	15–68								0.09–0.45	0.27
Greece	Different							0.033–0.1													
Italy	Different			20–307	95						14	4–81	26				16	0.4–2.2	0.9		
Netherlands	Sand								0.04												
	Clay							0.45–1.1													
Norway	Different							0.02–0.35	0.19							0.7–8.8	2.5			0.15–2.32	0.78
Poland	Sand	0.01–0.24	0.07	2–60	12	1–26	8.0			1–52	8	8.5–23.5	16	7–150	30	0.5–15	2	0.2–3.0	1.5	0.06–0.38	0.14
	Loess	0.24–0.36	0.30	21–35	29	8–54	19			7–70	19	14–32	26	20–130	50			0.6–3		0.17–0.34	0.23
	Clay	0.04–0.80	0.27	14–80	38					10–104	25	13–52	25			1.4–10	4.5	0.1–6.0	3	0.18–0.6	0.3
	Different			4–68	20			0.02–0.16	0.06	1.3–68	9					0.1–10.3	3.3				
Russia	Sand		0.32			1.5–29	11							4–57	30			0.3–2.9	1.5	0.05–0.32	0.18
	Loess					11–36[a]	25							40–55	50			1.8–3.3	2.2		
	Clay				51	4–21	12							9–77	35			0.6–4	2.0		
	Different							0.06–0.29	0.1									0.8–3.6	2.2		
Spain	Different							0.03–0.37	0.15								8.4				
Sweden	Different							0.004–0.99	0.06											0.17–0.98	0.39
UK	Sand			5–360	42					3.5–110	20					5.1–6.8				0.15–0.24	
	Loess											24–96[a]	63	67–180[a]	125						
	Clay	0.49–0.61					37											0.7–4.5	2.5		
	Different				69	11–323	23	0.01–0.09	0.03		23	15–41	29			4–95	16.3	1–5	1.2		0.21
USA	Sand	0.08–0.47	0.21	3–200	40	1–70	14	0.01–0.54	0.08	<5–70	13	<10–70	17	5–165	40	<0.1–30	5.1				0.5
	Loess	0.13–0.55	0.27	10–1000	55	7–100	25	0.02–0.32	0.06	5–30	17	10–30	19	20–110	60	1.7–27	7.7	0.75–6.4	2.5	0.02–0.7	0.26
	Clay			20–150	65	7–70	29	0.0–0.90	0.13	5–50	21	10–70	22	20–220	70			1.2–7.2	4.1	0.1–1.9	0.5
	Different					3–300	26									<1–93	7	0.8–3.3	2.0		

[a] Alluvial soils.

III.4.4.3.2. Regulatory limit values for heavy metals in sludge and soils

High concentrations of heavy metals in sewage sludge applied to land may pose a risk of accumulation through the food chain. However, not all metals in all soils, also the loads added to soil with sewage sludge pose the same hazard to the food chain. The differences between regulatory limit values for metal concentrations in biosolids and in soils within European countries, North America and New Zealand are remarkably high (Tables III.4.10 and III.4.11) and reflect the differences in approaches and protocols adopted to establish these values in view of soil protection.

These protocols for acceptable risk assessment can be summarized as below (after Amlinger, 1998):

- risk assessment based on no observable adverse effect levels (NOAELs);
- precautionary limitation or no net degradation (NND), adequate to a single safe threshold value – predicted no effect concentration (PNEC) or to a single predicted effect concentration (PEC);
- best available technique (BAT);
- hybrid systems utilizing toxicity assessments or embodying soil protection without quantifying risk.

Limit values of metals in biosolids and soils where biosolids are to be applied refer to a single total metal concentration. Among these regulations is *Directive 86/278/EEC (1986)*, currently under revision, which specifies the conditions under which sewage sludge can be used in agriculture within the European Union. On setting these limits, the maximum admissible concentrations in food and foodstuffs were determined after considering metal uptake by plants and crops, and metal phytotoxicity and zootoxicity data available at that time. In the EU, risk assessment for metals in the framework of the Existing Substances Regulation is based on a single PNEC or PEC value for soil organisms throughout Europe derived from total concentrations. The more stringent standards imposed by the national regulations by EC Member States are also allowed (Van den Berg, 1993).

In Canada, the responsibility of managing sewage sludge treatment and disposal lies within each province. In March 1996, the Ontario Ministry of Environment and Energy issued a set of *Guidelines for the Utilization of Biosolids and Other Wastes on Agricultural Land* (MOEE Ontario/MAFRA, 1996) that established limit values for 11 metals in sludge and soils, generally below the lower limit values for sludge and within the lower limit values for soils established by the EEC Sludge Directive (1986). Also in Quėbec standards have been set for acceptable levels of heavy metals in sludge and in fertilized soil. Only the total quantity of metals in the non-specified soils is considered in these standards, similarly to one given in the majority of other regulations (Tables III.4.11 and III.4.12).

In New Zealand, regulatory limit values of metals in biosolids are markedly below the lower values, while for biosolids-amended agricultural soils standards are mostly close to the highest values set by the EEC Sludge Directive (1986) and the European national regulations.

In 1993, the US Environmental Protection Agency published *Part 503 – Standards for the Use and Disposal of Sewage Sludge* (Goldstein, 1993; US EPA, 1993) and the US federal regulations governing sewage sludge (biosolids) land application were

Table III.4.10. Limit values for heavy metal concentrations in sewage sludge/compost in the EU, Canada, USA and New Zealand (mg/kg d.m.) (after Amlinger, 1998; Polish Directive of Minister of Environment on Sewage Sludge, 1999; EC DG ENV, 2000).

Country	Regulations	Cd	Cr_t	Cr(VI)	Cu	Hg	Ni	Pb	Zn	As	Co
EC/sewage sludge											
(86/278/EEC)	Lower limit	20	–	–	1000	16	300	750	2500	–	–
	Upper limit	40	–	–	1750	25	400	1200	4000	–	–
EC DG ENV.E3	Short term	10	1000		1000	10	300	750	2500	–	–
3rd Draft (2000)[a]	Medium term (~2015)	5	800		800	5	200	500	2000	–	–
	Long term (~2025)	2	600		600	2	100	200	1500	–	–
Austria	ON S 2200[b]										
	Class I[b]	0.7	70	–	70	0.7	42	70	210	–	–
	Class II[b]	1	70	–	100	1	60	150	400	–	–
	Class III[b]	4	150	–	400	4	100	500	1000	–	–
Belgium	Min. f. Agric.	1.5	70		90	1	20	120	300	–	–
Denmark	Sew. sludge	0.8	100	–	1000	0.8	30	120	4000	–	–
Finland	Trigger values[c,d]	3	300	–	600	3	100	150	1500	50	–
	Target values 1998[c,d]					1		100			
	Fertiliz. growing media				100	0.2	60	60	150	10	
France	Sew. sludge/ind. waste[e]	20	1000	–	1000	10	200	800	3000	–	–
	From 2001	15									
	From 2004	10									
Germany	M to Kl. I[b]	1.5	100	–	100	1	50	150	400	–	–
	M to Kl. II[b]	2.5	200	–	200	2	100	250	750	–	–
	RAL GZ 251[b]	1.5	100	–	100	1	50	150	400	–	–
	Blauer Engel[b]	1	100	–	75	1	50	100	300	–	–
	Biowaste ordinance I[f]	1	70	–	70	0.7	35	100	300	–	–
	Biowaste ordinance II[f]	1.5	100	–	100	1	50	150	400	–	–
Greece[d]		–	–	–	–	–	–	–	–	–	–
Ireland	Sew. sludge, agric. use	20	–	–	1000	16	300	750	2500	–	–
Italy	DPR 915/82	10	500	10	600	10	200	500	2500	10	–
	Ann. 748/84 green comp.	1.5	–	0.5	150	1.5	50	140	500		
Italy[d]		1.5	–	100	1.0	75	100	300	–	–	–

Luxembourg[d,g]	Recommended	20	1000	–	1000	16	300	450	2500	–	–
	Limit values	40	1750	–	1750	25	400	1200	4000	–	–
The Netherlands[h]	Compost	1	50	–	60	0.3	20	100	200	15	–
	Compost (very dean)	0.7	50	–	25	0.2	10	65	75	5	
Portugal[d]		–	–	–	–	–	–	–	–	–	–
Sweden[d]		2	100	–	600	2.5	100	100	800	–	–
	Guideline of QAS	1	100	–	100	1	50	100	300		
Spain	Decr. 1310/1990 pH > 7[d]										
	pH > 7[d]	40	1500	–	1750	25	400	1200	4000	–	–
		20	1000	–	1000	16	300	750	2500		
	B.O.E. n'm. 131, 06.1998	10	400	–	450	7	120	300	1100	–	–
United Kingdom	Sew. sludge/pasture land	–	–	–	–	–	–	1000	–	–	–
	UKROFS fertil. org. farm.	10	1000	–	400	2	100	250	1000	–	–
Poland[d]	Direct. Min. Envir. 2002:										
	Agricultural use	10	500	–	800	5	100	500	2500	–	–
	Non-agric. land reclam.	25	1000	–	1200	10	200	1000	3500	–	–
	Plants f. comp., land stab.	50	2500	–	2000	25	500	1500	5000	–	–
Canada[d]		20	–	–	–	5	180	500	1850	75	150
USA[d,i]	EPA/high quality	39	(1200)	–	1500	17	420	300	2800	41	
	EPA/others	85	3000	–	4300	57	420	840	7500	75	
	Composting Counc. 1996	39	–	–	1500	17	420	300	2800	41	
	Rec. USDA-Min. f. Agric.	21	–	–	–	–	–	–	–	54	
New Zealand		15	1000	–	1000	10	200	600	2000	–	–

[a]In parallel, limit values for amounts of heavy metals, which may be added annually to soil are given, based on a 10-year average (g/ha/yr) – numerically a triplicate of adequate limit values.
[b]Referring to 30% o.s.
[c]Soil improver and compost products.
[d]Limit values for application of sewage sludge.
[e]Cr + Cu + Zn max 4000 mg/kg d.m.o.
[f]Related to maximum application rate of 20 and 30 t d.m./ha.
[g]In preparation: values referring to RAL GZ 251.
[h] > 20% o.s. in d.m.
[i]For all organic waste.

Table III.4.11. Limit values for heavy metal concentrations in the soil comparing the EU, Canada, USA and New Zealand (mg/kg d.m.) (after Smith, 1994; Amlinger, 1998; Polish Directive on Sludge, 1999; EC DG ENV, 2000).

Country	Regulations	Cd	Cr	Cu	Hg	Ni	Pb	Zn	As	Mo	Se
EC/soil amended with sludge											
(86/278/EEC)	Lower limit	1.0	100[a]	50	1.0	30	50	150	–	–	–
	Upper limit	3.0	150	140	1.5	75	300	300	–	–	–
EC DG ENV.E3	5 ≤ pH < 6	0.5	30	20	0.1	15	70	60	–	–	–
3rd Draft (2000)	6 ≤ pH < 7	1.0	60	50	0.5	50	70	150	–	–	–
	pH ≥ 7	1.5	100	100	1.0	70	100	200	–	–	–
Austria	ON L 1075	1.0	100	100	0.7	60	100	300	–	–	–
Belgium	Flanders[b,c]	1.2	78	109	1.3	55	120	330	–	–	–
	Wallonia[b]	1.0	100	50	1.0	50	100	200	–	–	–
Denmark		0.5	30	40	0.5	15	40	100	–	–	–
Finland[b]		0.5	200	100	0.2	60	60	150	–	–	–
France[b]		2	150	100	1.0	50	100	300	–	–	–
Germany[d]	Clay	1.5	100	60	1	70	100	200	–	–	–
	Loam	1	60	40	0.5	50	70	150			
	Sand	0.4	30	20	0.1	15	40	60			
Greece		–	–	–	–	–	–	–	–	–	–
Ireland		1.0	–	50	1.0	30	50	150	–	–	–
Italy		3.0	[e]	100	2.0	50	100	300	–	–	–
Italy[b]		1.5	–	100	1.0	75	100	300	–	–	–
Luxembourg[b]	Recommended	1.0	100	50	1.0	30	50	150	–	–	–
	Upper values	3.0	200	140	1.5	75	300	300	–	–	–
The Netherlands[b]		0.8	100	36	0.3	35	85	140	29		
Portugal		–	–	–	–	–	–	–	–	–	–
Sweden[b]		0.4	30	40	0.3	30	40	75	–	–	–
Spain	1310/1990 pH > 7[b]	3.0	150	210	1.5	112	300	450	–	–	–
	pH > 7[b]	1.0	100	50	1.0	30	50	150	–	–	–
United Kingdom[b,e]		3.0	400[f]	135[g]	1.0	75[g]	300	300[g]	50	4	3
	UKROFS	2.0	150	50	1.0	50	100	150	–	–	–

Poland	Agricultural use soils										
	Heavy	3	100	75	1.5	50	80	180	–	–	–
	Mean	2	75	50	1.2	35	60	120	–	–	–
	Light	1	50	25	0.8	20	40	80	–	–	–
	Non-agricult. use soils										
	Heavy	5	200	100	2	60	100	300	–	–	–
	Mean	4	150	75	1.5	45	75	220	–	–	–
	Light	3	100	50	1	30	50	150	–	–	–
Canada		2.0	–	–	0.5	18	50	185	7.5	2.0	1.4
USA[h]											
EPA Part 503 Rule	Soils – upper limit	19.5	1500	750	8.5	210	150	1400	20.5	9	50
EPA: risk-based concentrations (RBC)	Soils – residential area	39 n	Cr(III) 78,000 n, Cr(VI) 390 n	2900 n	23 n	1600 n		23,000 n	23 n	390 n	390 n
	Soils – industrial area	510 n	Cr(III) 100,000 n, Cr(VI) 5100 n	38,000 n	310 n	20,000 n		310,000 n	310 n	5100 n	5100 n
New Zealand		3.0	600	140	1.0	35	300	300	–	–	–

[a]Planned.
[b]Limit values for application of sewage sludge.
[c]Soil with 10% clay and 2% OM.
[d]Compost ordinance.
[e]Cr(VI) 3 mg/kg and Cr(III) 50 mg/kg.
[f]Preliminary.
[g]Soil pH 6.0–7.0.
[h]EPA Part 503 Rule and EPA Region III risk-based concentrations (n – non-carcinogenic).

Table III.4.12. Classification of organic substances with respect to their behavior in soils (source: Langenkamp et al., 2001a, cit. after UMK-AG, 2000).

Substance	Mammalian/human toxicity (acute)	Ecotoxicity	Water solubility	Persistence	Concentration levels[a]
AOX (summative parameters)					High, indicator
LAS	Medium	Aquatic high, terrestrial medium, bioaccumulation high	High, enhances mobility of other pollutants	Medium	High
DEHP	Low, suspected estrogenic effect	Aquatic medium/high, terrestrial low, bioaccumulation high	Low	Medium	High
Nonylphenol	Medium, suspected estrogenic effect	Aquatic high, terrestrial medium, bio accumulation high	Low	Medium	High
B(a)P single substance, PAH	Carcinogenic, mutagenic, teratogenic	High, bioaccumulation high	Low	High	High
PCBs, single substance/summative parameters	Medium, tumor promoting, immunotoxic	Aquatic high, terrestrial high, bioaccumulation high	Low	High	Low and declining
PCDD/Fs, single substance/ summative parameters	High, carcinogenic	Aquatic high, terrestrial high, bioaccumulation high	Low	High	Low
TBT, tributylin oxide	High	Aquatic high, bioaccumulation high, endocrine effect	Medium	High	High

[a]In the EU Member States. In other countries may be different, depending on generation and source control.

promulgated. The rules provide minimum risk-based standards for chemicals, among them for nine inorganic elements. To develop the standards, a risk assessment that examined 14 pathways of exposure to people, agricultural crops, livestock and selected environmental receptors was performed. These standards may be supplemented by stricter state and local rules (Goldstein, 1993, 2000; Harrison and McKone, 2002). Compared to limit values in force in the EU and other countries, general similarity of the US standards for high quality biosolids (Table III.4.11) and strikingly higher values for amended soils (except Pb), up to an order of magnitude (Table III.4.12) illustrate the difference of the US EPA approach to the target risk receptor, which is human, while ecological multifunctionality of soils is not adequately addressed in these rules.

On setting almost all these standards, little account was made for the possible effects of metals on the soil microbial population (McGrath et al., 1995; Weissenhorn et al., 1995). Alarmingly, studies initiated since the beginning of the last decade of 20th century have revealed adverse effects due to metals on soil microbial populations and their activities at concentrations close to EC limits for sludge application (Wild et al., 1990; Wang and Jones, 1994; Witter et al., 1994; Weissenhorn et al., 1995). A lack of long-term data and experiments aimed at assessing the effects of metals added to soils in sewage sludge over extended periods of time were also noted (McGrath et al., 1995), though since then a considerable progress in this area has been achieved (McGrath et al., 1999, 2000, 2003; McGrath, 2002). In some cases, environmental damage has been noticed years after a previously thought safe material had been used on the soil.

In the last decade, it has became obvious that criteria and standards regarding the maximum permitted concentrations of metals in soils virtually in all regulations (Table III.4.11), which are based on measurements of total concentration as determined by acid digestion, may not provide the best indication of its bioavailability. Numerous investigations have revealed that the total metal content neither correlates with its availability to crop plants and soil organisms, nor does it show how the metal is bound in the soil (e.g. Hooda and Alloway, 1994; Badilla-Ohlbaum et al., 2001; Ginoccio et al., 2001; Allen, 2002a,b).

It has also become evident that the reliance of the current standards on risk assessment methods consistent with the guidelines developed in late 1980s (Directive 86/278/EEC) and early 1990s (U.S. EPA, Part 503), and relying on a sewage sludge/soil survey dating from these periods are now outdated. Controversies surrounding both the practice of land application and the science behind the regulations, as well as evidences of adverse health effects of sewage sludge use (NRC, 2002), along with the prospects of a significant increase of sewage sludge generation and use in the nearest future, moved both the European Commission and US EPA to commissioning broad expert studies in 1999–2002 in order to update an information on current status of pollutants in sewage sludge and soils and to review current scientific knowledge concerning pollutant transfer mechanisms in the different environmental compartments and in the food chain, aiming to assess the possible risk to the environment and human health in accordance with this knowledge. Most of the studies commissioned by the European Commission have been discussed in this chapter. The comprehensive analysis of advances in risk assessment since the establishment of the Part 503 Rule, evaluation of EPA's approach to setting chemical and pathogen standards and conclusions suggesting integration of chemical and pathogen risk assessment have been presented in the study performed for US EPA by the Committee on

Toxicants and Pathogens in Biosolids Applied to Land of the National Research Council of the National Academy of Sciences. In particular, aggregate exposure assessments with special consideration to risks from long-term low-level exposures, as well as short-term episodic extremes have been recommended (NRC, 2002).

Reviews of reference sources on mechanisms affecting metal transfer in soils, also amended with sewage sludge, have brought to the conclusion that among the factors influencing metal mobility and bioavailability to plants, soil microorganisms and other soil biota, pH level of the soil is the most important; the role of binding to organic matter and mineral fraction in metal accumulation in the upper layer of the soil is also of crucial importance. Soil organic matter together with clay minerals makes up the most of cation exchange capacity (CEC) that has been considered to be a key parameter determining the metal sorption by soil (Balze et al., 1999; ANDERSEN-SEDE, 2001).

The common awareness of inadequacy of existing soil quality standards based on total metal concentration values leads to the revision of old standards in order to development of new ones that intend to adopt recent sound scientific information to derivation of relevant Environmental Quality Criteria (EQC), which define safe concentrations of chemicals in soils that would not affect the structure and function of terrestrial and boundary ecosystems both in short- and long-term span. In more recent regulations including Working document on sludge (EC DG ENV, 2000), limit values are related to the parameters considered critical for metal mobility and bioavailability in soil: pH (EC Working document on sludge) or soil type reflecting organic matter (OM) and clay mineral enrichment, e.g. German Compost Ordinance and Polish regulations (Table III.4.12).

III.4.4.3.3. Novel concepts of risk assessment for metals in soils

It, though, becomes evident that incorporating into regulatory values the parameters influencing metals mobility is not enough for prevention of heavy metal risk for soil and for boundary ecosystems and that the science-based EQC, besides chemical processes, should consider also physiological aspects for reliable predicting metal bioavailability and toxicity (Janssen et al., 2003). A generic definition of "bioavailability" of chemicals of concern *refers to a fraction of the total contaminant mass in soil/sediment available to receptor organisms, including human and ecological organisms* (Adriano, 2003; NRC, 2003). Metals and metalloids bioavailability approach deals with kinetic processes of *lability* transformation while their total mass remains unchanged. Metal lability, partitioning and its relation to bioavailability in terrestrial ecosystems, risk assessment and risk management have been widely discussed in relevant comprehensive publications (Gupta et al., 1996; Adriano, 2001, 2003; Allen, 2002a,b; NRC, 2003); some basic terms and processes are summarized here briefly.

The bioavailability of metals depends on chemical form of their occurrence in soils or *speciation*. Soils are dynamic systems, in which a very unstable equilibrium exists between the labile bioavailable fraction, the mobilizable fraction (potentially bioavailable, moderately leachable and partly active) and immobile, strongly bound inactive fraction. Ecological risk assessment is a fundamental consideration to evaluate the effects of metals in soil specific to risk receptors dependent upon the magnitude, frequency and duration of exposure. Exposure assessment is based on the direct interactions of soil organisms and plant roots with bioavailable heavy metal fractions. The human health risk assessment should thus take into account several pathways, of which the food chain via plants plays the major role, either directly through food crops or indirectly via farm animals. Additionally, the direct ingestion of soil particles by small children and grazing animals (when dissolution of metals in strongly acidic intestinal fluids takes place) should be considered. The risk of metals in soil to hydrosphere, mainly to groundwaters, depends predominantly on the leaching process, where the vertical metal transport through the vadose zone and its further migration in saturated zone result both in the mobilization of the labile metal fraction and its immobilization due to pore solution–soil interaction during transport. It can be thus concluded that the key role in protection of ecological soil function and attenuation of metal uptake through food chain plays science-based predicting metal bioavailability and toxicity to sensitive soil organisms (microbes, invertebrates) and plants.

The most labile and readily bioavailable fractions are represented by the soluble metal components occurring in soil pore solution as free ions or soluble complexed ions (ion pairs or complexed with humic ligands), ions that are weakly adsorbed on exchange surfaces in soils or bound by carbonates. Biogeochemical mobilization/immobilization processes of different kinetics that determine metal *partitioning* between aqueous and solid phases of different binding strength comprise desorption/adsorption, dissolution/precipitation, complexation, redox reactions and complex processes termed as weathering and fixation in immobile phases (e.g. in humins, crystal lattice). These processes are influenced by a variety of chemical, physical and biological factors, such as pH, dissolved and solid-phase organic matter and its chemical speciation, carbonate and metal oxide (Fe, Al, Mn) content, sulfides, clay minerals, secondary phases, redox potential, time-related weathering transformations, microbial sequestration/oxidation, etc. The variability of factors controlling the binding strength of soils for metals and partitioning process are largely a consequence of difference in soil properties (Adriano, 2001, 2003; Allen, 2002a,b; Impellitteri et al., 2002; Yin et al., 2002; NRC, 2003).

The partitioning may be modified in the rhizosphere and within the digestive tract of soil-dwelling organisms. It may change over time because of natural or anthropogenic processes, e.g. as a consequence of the application of sewage sludges to soil (Allen, 2002a). The modifications in metal partitioning in sewage sludge-amended soil may occur partly due to probable presence in sewage sludge of non-humic ligands that come from proteins and other biological macromolecules, which were considered to be a possible explanation of observed much higher concentrations of strong ligands in wastewater effluent compared to those in natural organic matter in river water (Sarathy and Allen, 2003). Similar relation may occur also between ligands in sewage sludge and soil.

Schematics of bioavailability processes in soils exemplified in metal uptake by plants are depicted in Figure III.4.3.

Phase (A) comprises metal partitioning and its release to soil solution: Phase (B, B′) involves transport of metal to the target organism in soluble, colloidal and particulate form. Phases (C) and (D) delineate bioavailability processes. Phase (C) involves metal passing through organism–soil/pore solution interface that constitutes a biological membrane, which serves also as a bio-filter for contaminants (Adriano, 2003; NRC, 2003). In plants, metals pass through the roots membrane (McLaughlin, 2002). Intestinal metal uptake and internal metal partitioning that involve digestive fluids have been considered to be a dominating metal exposure route for invertebrates, in particular for hard-bodied ones, though dermal uptake has been found in some cases to correlate better (Allen, 2002a,b,

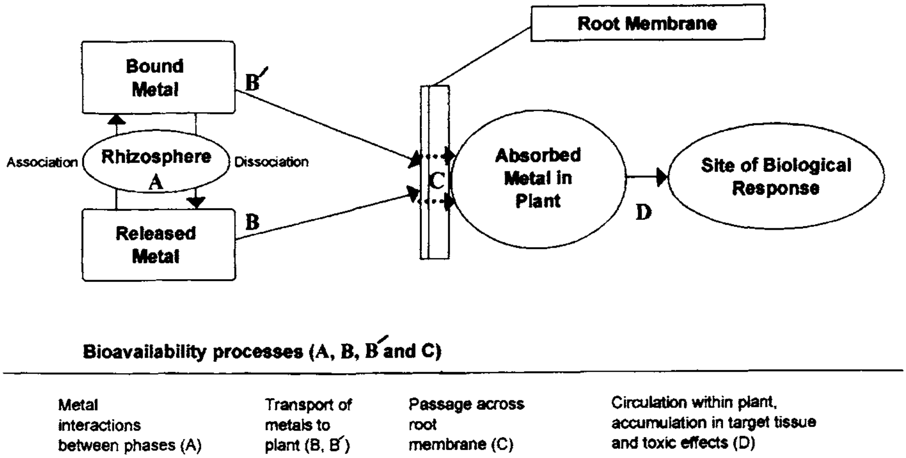


Figure III.4.3. Bioavailability of heavy metals in soil exemplified in plants (after Adriano, 2003; modified from the NRC, 2003).

Peijnenburg, 2002). Also some recent reports (Vijver et al., 2003a,b) support a conclusion about predominance of a dermal uptake by soft-bodied species. Phase (D) delineates assimilation of a metal in the organism and its biological response at the site of toxic action (Peijnenburg, 2002; Adriano, 2003).

It is clear that while metal mobility and bioavailability to plants and organisms in soils are determined by the kinetic processes and depend on the variable physical and chemical soil properties and different uptake mechanisms, risk assessment based on a single value and total metal concentration alone leads to false-positive or false-negative estimation of risk to site-specific terrestrial ecosystems. There is thus a must to develop regulatory programs and predictive models that consider metal bioavailability. Such programs are of particular importance in view of inevitable world's increase of anthropogenic impact on the terrestrial ecosystems in the 21st century due to growth of sewage sludge generation in parallel with increase of its use as soil amendment, as it has been already observed in the EU and in the USA.

As more definite evaluation of bioavailability becomes available, it should be incorporated into soil screening levels, criteria and soil quality standards, with a general aim to protect specific sites, specific processes, or life support functions within the terrestrial ecosystems based on prediction of actual effects. Although to date bioavailability-based approach is gaining wide acceptance, at present the understanding of factors that control bioavailability of metals in soils in the short and long term is still incomplete. The consideration of both chemistry and biology is the major requirement to advance developing sufficiently robust predictions of metal bioavailability in soils that can be incorporated into the regulatory programs (Allen et al., 2002; Schoesters et al., 2003).

Recently developed models for predicting metal concentrations in plants and soil organisms using soil property measurements seem to be promising, also for biowaste-amended soils, in particular the development and adaptation to the terrestrial systems of the aquatic biotic ligand model (BLM), which combines chemical speciation models with more biologically oriented models. BLM has given rise to mechanistic understanding of the partitioning and uptake kinetics for metals from soils and enabled to evolve information on the relationship of appropriate soil parameters and organisms' responses (Cheng and Allen, 2001; Di Toro et al., 2001; Allen, 2002a,b). BLM development, principles and the potential of BLM approach are discussed in detail by Janssen et al. (2003). Novel models describing trace metal concentrations in the earthworm, *Eisenia andrei*, and in selected cultivated plants have been proved to have a considerable potential to be used in predicting metal bioavailability to soil organisms in polluted and sewage sludge amended soil. Model parameters quantify biological phenomena important for metal bioavailability, while soil variables quantify relevant soil chemistry characteristics. Of four metals studied (Cd, Cu, Pb and Zn), the model appeared the most accurate in describing Zn behavior (Saxe et al., 2001).

Through the application of the BLM principles, it becomes possible to facilitate the collection of the necessary data to evaluate the relationship between soil parameters and organisms responses and to predict the bioavailability of metals in different soils (terrestrial BLMs or t-BLMs) that would meet the needs of industry and regulators (Allen and Santore, 2003; Schoesters et al., 2003).

In parallel to development of soil BLMs (e.g. Allen and Santore, 2003; Peijnenburg et al., 2003; Van Gestel and Koolhaas, 2003), the current extensive research activities are focused on evaluation of mechanisms of time-dependent changes in metal speciation, and on the dynamic nature of bioavailability resulting from changes in input to the environment or in modifying factors (e.g. Hiemstra et al., 1996; Yin et al., 1997; Kinniburgh et al., 1999; Allen and Ponizovsky, 2003; Gustaffson et al., 2003; Ponizowsky et al., 2003; Ponthieu et al., 2003; Shi et al., 2003). Process kinetics and underlying mechanisms are of particular importance for long-term prediction of metal uptake in anthropogenically affected (e.g. sludge amended) soils.

The chemical methods of metal speciation by sequential fractionation developed in the last two decades to estimate chemical forms of binding, and particularly single extractant procedures (with use DTPA, EDTA, acetic acid, and the mineral acids HNO_3 or HCl) to assess metal bioavailability, appear to fail to precisely identify chemically specific soil fractions and to correlate them with bioavailability, thus their usefulness for these purposes is limited (Sauvé, 2002, 2003). Sequential chemical extraction is a useful tool for identification of operationally defined soil pools of different binding strength and metal mobility. For defining bioavailability (phases C and D – Figure III.4.3), i.e. the rates of metal supply from soil/pore solution through biological membrane (phase C) to the chosen biological endpoint (phase D), other approaches are needed. Soil-solution free metal ion activity as a parameter to estimate bioavailability and the free ion activity model (FIAM) based on this parameter offer a promising alternative approach, though further integrated chemical and biological research are required to explain biological responses and to combine them with chemical determination of free metal ion activities (Allen, 2002a,b; Sauvé, 2002).

In this case, a novel method of diffusive gradients in thin films (DGT) simulating metal passage through organism–soil/pore solution interface offers an excellent tool to quantify metal bioavailability (Zhang et al., 2001; Fitz et al., 2003; McGrath et al., 2003). Besides, it was found of importance also to segregate and consider separately metal uptake (phase C) and metal toxicity, i.e. toxicological bioavailability based on internal recirculation and storage processes of the metals assimilated, resulting in transport to the target sites of toxicity (phase D) (Adriano, 2003; Peijnenburg et al., 2003).

At present, extensive studies on the determination of toxicity thresholds of metals for plants, microbes and invertebrates have been carried out, both in view of practical application of equilibrium partitioning and bioavailability concepts (e.g. Zhang et al., 2001; Criel et al., 2003; Fitz et al., 2003; Peijnenburg et al., 2003) or using more conservative PNEC (Smolders et al., 2003) or ecological soil screening levels (ECO-SSLS) approach (Checkai et al., 2003).

III.4.4.3.4. Effect of sewage sludge on metal bioavailability in amended soils

Metal enrichment in sewage sludge, high organic matter content of possibly partly different nature than that of natural origin (Sarathy and Allen, 2003), and instability of sewage sludge that undergoes "aging" transformations over time, influence the properties of amended soils, which results in alteration of the fractionation with respect to binding strength for metals, partitioning of metals to the soil, their bioavailability to microbes, soil animals and plants and further transfer through the food chain.

Even when the soils are greatly enriched, some metals (e.g. As, Cr(III), Hg and Pb) have been shown to sorb to and bind to solid phases in soil and soil colloids, removing the metals from pore solution and rendering them unavailable to higher trophic levels. They may also be retained in plant roots. Although plants are able to uptake certain metals, phytotoxicity may maintain plant concentrations of these elements (B, Cu, Mn, Ni and Zn) below safe levels for animals. When heavy metal concentrations in plant tissue are maintained at levels deemed safe for animals by one or more of these processes, the food chain is said to be protected by a "soil–plant barrier". This soil–plant barrier has been found to be effective for the heavy metals of concern in sewage sludge, with the exception of Cd, Mo, Se, and possibly Co, which are readily adsorbed and translocated to food-chain plant tissue (Chaney, 1980). Evidence indicates that Mo, Se and Co seldom occur in large enough concentrations to cause problems.

It would seem that Cd is the heavy metal of most critical concern, and that its content in sewage sludge is one of the key elements in determining whether or not the sludge is useable in agriculture (EC DG ENV, 2000). The uptake of cadmium by plants varies greatly from crop to crop and this should be reflected in agricultural management practices. In addition, plants are capable of taking up and concentrating relatively large amounts of Cd without, or practically without, harm to themselves. However, these high concentrations may render the plants unsuitable for human consumption.

Despite extensive experimental efforts, there is still a controversy over the possible long-term effects of sludge applications and leaching, in particular over the antithetic "sludge protection" thesis that launches the sludge adsorption properties in controlling metal lability and bioavailability and "time bomb" thesis stressing the hazard of metal release due to organic matter decomposition after terminating sewage sludge application (Chang et al., 1997). The recent studies rather do not support the "time bomb" concept based on the assumption that the major binding phase in sewage sludge is organic matter. There is an evidence that the substantially increased Cd binding associated with biosolids application is not limited to the organic matter but to the great extent results from the sorptive properties of Fe and Mn inorganic phase in sludge, thus the alteration in soil metal chemistry and phytoavailability is of a more persistent nature (Ryan et al., 2002). On this basis the authors concluded that reduction in phytoavailability justifies comparatively high limit values for Cd in sludge-amended soils established by the US EPA as adequately protective for human health and the environment (see Table III.4.12).

Research focused on competitive role of Zn in sewage sludge at normally low Cd:Zn ratio and the effect of Zn–Fe–Ca malnutrition in the consumers' diet showed that low Cd and low Cd:Zn ratio in biosolids reduce phytoavailability in aerobic soils and inhibit food-chain transfer and bioavailability of Cd, preventing Cd risk to consumers, regardless of the fraction of diet grown on biosolids-amended soils. It was found though that risk to humans from Cd uptake by crops should be considered at high Cd:Zn ratios, as well as for rice or tobacco grown on paddy soils, also when normal geochemical low Cd:Zn ratio occurs, in particular at low Zn–Fe–Ca diet (Chaney et al., 2002).

Long-term studies by McGrath et al. (2000) indicated that sludge application in the UK arable soils resulted in an increased bioavailability and crop uptake of Cd. Data reported by other authors confirmed Cd enrichment in soils amended with sludge, in particular labile ($>10\%$ Cd_t) and bioavailable forms (up to $>5\%$) (Afyun et al., 2003), sharply increased Cd content in maize and wheat shoots grown in such soils (Hylander and Souta, 2003; Green and Tibbett, 2003), and Cd bioaccumulation in herbivorous invertebrates, though considerably lesser mobility of Cd than of Zn in the food chain soil–plant (wheat)–aphid was observed (Merrington et al., 1997; Green and Tibbett, 2003).

The long-term field trial of clay loam soil in Sweden, which received sewage sludge biennially for 41 years, appeared to accumulate 92% of input load of Cd in topsoil 17 cm thick. Compared to unamended soil, soluble Cd was 20 times higher, and its concentration in straw about 2 times higher, with no significant trends over time. Direct measurements and scenario simulations with use of a model called SLAM to illustrate trends in Cd availability during sludge application and its following cessation demonstrated that the environmental behavior of this system according to "sludge protection" or "time bomb" concept depends on Cd input rate, sludge/soil sorption capacity and the proportion of inorganic binding phase in the total sorption capacity of sludge, with pH as a major controlling factor (Bergkvist and Jarvis, 2003; Berkvist et al., 2003). In the light of the presented data, the "time bomb" concept seems to be unrealistic unless a drastic pH change occurs, while the extent of "sludge protection" function is determined by Cd partitioning.

These results that give an evidence of possible reduction of safety level mostly due to overloading a specific system with Cd, suggest higher precaution and lesser generalization with respect to risk from Cd in different sludge-amended soils. Recently developed simple model for predicting Cd concentrations in wheat grain using regulatory total limit concentrations of Cd in sludge-amended soils modified by the factors affecting bioavailability in different soils (soil pH) and incorporating a cultivar term into the model seems to be promising (McGrath et al., 2002).

Zn is another metal that should be strongly considered due to abundance in sewage sludge, higher bioavailability and transfer in food chain, despite of far lesser toxicity than Cd (McGrath et al., 2000). On the other hand, Zn presents the principal potential risk from phytotoxicity and adverse impact on soil microbes (McGrath, 2002; McLaughlin, 2002). Investigations of temporal and management-induced changes in the sewage sludge-derived Zn in a sandy pasture soil showed 5–7-fold increase of mean Zn concentrations in pasture roots and 6–8 higher Zn content in the herbage, at scarcely 12–42% higher total Zn concentrations in sludge-amended soil than in unamended one. A substantial proportion (19–17%) of Zn load reached the shallow groundwater over the 4 years' application of sludge. Very high Zn mobility was found to be compatible with high soil solution concentrations in the amended low-pH soil (Speir et al., 2003). Long-term (6 years) experiments on acidic soil amended with metal-spiked sewage sludge confirmed similar much higher proportion of Zn enrichment in the mobile and mobilizable fractions, and in pasture herbage than in control soil, and strong effect of pH on Zn bioavailability (McLaren and Clucas, 2001, 2003). Sewage sludge derived Zn was found to readily biomagnify in the food chain exemplified in the soil–wheat–aphid system: concentrations in sap feeding herbivore appeared to be 1.4–2.4 times higher than in the shoots (Merrington et al., 1997; Green and Tibbett, 2003).

Other potentially dangerous elements (PDEs) in sewage sludge-amended soils also received attention of researchers. In general, Ni seems to behave similarly to Zn. Long-term (6 years) experiments with use of acidic soil treated with unspiked and spiked by Cu, Ni and Zn sewage sludge, were reported to show stable (at least 3 years long) higher proportion of all three metals enrichment in mobile and mobilizable phases and substantial increase of Ni and Zn concentrations also in herbage cover in spiked sewage sludge. This observation suggests insufficiency of "aging" for simulating actual kinetics of equilibration processes and thus possible erroneous predictions based on parameters measured on "aged" material. The pH control by liming resulted in declining Ni and Zn concentrations in herbage that confirm pH to be a major factor controlling Ni availability to plants (similarly to Zn), while Cu concentrations in herbage cover appeared neither to be significantly affected by sludge applications, nor by pH control measures (McLaren and Clucas, 2001, 2003).

The change of Pb content in maize (grain and shoots) was found insignificant as a consequence of the application of biosolids to clay and sandy soils of pH 5.7 up to total rate 50 t/ha over a period of 5 years (10 t/ha year) that confirms strong sorption of Pb by soil colloids and weak translocation to aboveground tissues. Though, even this low rate of biosolids caused an increase of total Pb concentration in both soils and downward movement in sandy soil. This leads to the conclusion that biosolid application may lead to elevated Pb accumulation in soils, up to maximum regulatory levels (Oliviera et al., 2003).

There is considerable variance in the metal content of different plants and different plant parts. For example, most vegetative parts, particularly leaves, are moderately high in metals, while seeds, nuts and fruits are normally low. It has been found that both crop yields and metal concentrations in soil become greater with increasing sludge loadings. The latter correlation suggests a complex system of microbial action, solubility and diffusion.

Observations of effects of a high dose (388 t/ha) sewage sludge application in clay and sandy tropical soils within 1 year before the first plantation of grass (*Bracharia brizantha*) on Cr, Cu, Ni and Zn concentrations in soil, grass biomass and metal uptake seem to be of interest, and can be summarized as follows: (i) the addition of sewage sludge resulted in over 10 times higher Cr, Cu, Ni and Zn content in the clay soil and 3–10 times higher metal concentrations in sandy soil; (ii) in two consecutive years grass biomass was 40% and 3.3 times higher in clay soils and 80% and 2.7 times higher in sandy soil, respectively, than in unamended soils, but in the following years turned to be lower due to depletion of nitrogen, and required fertilization; (iii) Despite several times higher concentration of metals introduced to the soils by application of sewage sludge, the total difference in plant uptake was less than 1% for Cu and Zn for all the following trials (Matiazzo et al., 2003).

These purposely presented in detail results of a trial lead to the not very optimistic conclusion about (i) persistence and possible high level of metal contamination of soil from sewage sludge application; (ii) temporary fertilization effect; (iii) immensely long time needed to get visible effects of phytoremediation, even if more efficient specially selected plants are used. Besides, there is always a problem with a safe utilization of such metal harvesters.

As time passes following sewage sludge application, it is typical to observe a decrease of metal concentration in the plants grown on these soils that in turn indicates decrease of phytoavailability. It may not protect, though, soil microflora and organisms ingesting soil. Only singular 1-year application of the relatively uncontaminated sewage sludge in low doses (2.5–10% by weight) was reported to have no significant effect on metal concentrations in amended soils and their uptake by plants (Uri et al., 2003).

Metal transfer predictions estimated on a 1-year basis presented in the EU studies (ANDERSEN-SEDE, 2001) state that "metals brought to soil by sludge application represent a very low proportion of the amount of metals present in soil before sludge application" that differs from the data obtained from the long-term studies reported above. The same predictions vary greatly with respect to the number of years required before a limit value is reached for metal accumulation in sludge-amended soil, from 4500–34,000 years range in low accumulation scenario to 20–140 years range in the high accumulation scenario.

III.4.4.4. Organic contaminants transfer in sewage sludge-amended soils

The recent studies commissioned by EC show that limited data are available on the relative importance of contamination sources. Organic compounds applied to soil with sludge undergo various physical, chemical and biological transformation and translocation processes. Sparse data are at present available on the formation of intermediate compounds, as well as on the degradation kinetics and pathways of organic contaminants in soil (ANDERSEN-SEDE, 2001; ICON, 2001; Langenkamp et al., 2001a). Behavior of the major groups of organic substances in soil is overviewed in Table III.4.12.

The hormone steroids in soils were reported to degrade rapidly in laboratory incubations: estimated half-life of E2 was less than 0.5 days, when it was abiotically transformed into estrone (E1). E1 and EE2 were found to degrade microbially. The half-life of EE2 ranged from 3 to 7.7 days. However, the behavior and persistence of E1 in the soils are unknown (Colucci and Topp, 2001; Colucci et al., 2001). Although estrogenic steroids were reported to degrade rapidly in soils, their pathways in soils and groundwater and factors influencing their degradation remain unclear. Besides, little data are available on androgens widely used in livestock in some countries as growth promoters, which have become a recent public concern (Ying et al., 2002a). All the metabolites of widely used aromatic surfactants (alkylphenols and APE), of higher toxicity than the parent substances (nonylphenol NP, octylphenol OP, bisphenol A – PPA and AP mono- to triethoxylates NP1, NP2 and NP3) were found to demonstrate a very fast decrease within the first month, but all of them exhibited residual concentrations after 320 days (Marcomini et al., 1989;

Topp and Starratt, 2000): their persistence in Table III.4.12 is thus defined as medium. Little is known on the uptake of APEs and their degradation products both by plants and domestic animals (Ying et al., 2002b). Balance calculations showed that in Germany through the agricultural application of sewage sludge, soil is contaminated annually with 0.8 t OP, 16.5 t NP and 1 t BPA (Gehring et al., 2003).

Sorption of veterinary pharmaceuticals (tetracyclins, macrolids and sulfonamids) to soils strongly depends on the chemical itself, soil type, pH and ionic strength, e.g. sorption coefficient alteration factor due to pH is of 5–15 range. The most mobile appear to be sulfonamide compounds (Ter Laak et al., 2003). Sorption of several tested human pharmaceutical compounds also showed variability with the compound and soil type and seemed to correlate positively with the organic carbon content of the soil. Ofloxacin was reported to be strongly sorbed by soil, while clofibric was weakly bound (Drillia et al., 2003). Considering immense variety of human and veterinary pharmaceuticals of different chemical composition determining their persistence and mobility in soil and food chain, no general conclusions can be derived.

The review of the available data from literature sources performed by the EC and issued recently, which is aimed to evaluate hazard to groundwater, plants, soil organisms, animals and human from organic contaminants introduced with sludge to soils, can be summarized as follows (ANDERSEN-SEDE, 2001).

III.4.4.4.1. Hazard to ground and surface waters

The hazard of organic contaminant leaching to groundwater from the sludge-amended soil is greatly reduced, on one hand, by strong binding of persistent compounds (PCDD/F, PCB) to soil, and on the other hand, by high degradability in soil and short half-life of many organic compounds. Nevertheless, in the case of highly permeable light soils and a shallow water table, such risk cannot be neglected, in particular with respect to contaminants with longer half-life values. LAS, nonylphenols and TNT compounds show higher mobility; PAH compounds are also frequently detected in shallow aquifers. Run-off may play an important role in contaminant transfer, also with soil particulates, enriching river sediments and posing risk to the aquatic environment.

III.4.4.4.2. Hazard to microorganisms

Soil microorganisms are considered to be adaptable to organic contaminants introduced to soil with sludge, though in many cases there is no definitive evidence of lacking adverse effects on soil microflora, in particular of emerging pollutants.

III.4.4.4.3. Hazard to plants

Most organic pollutants are not uptaken by plants from the sludge-amended soil. A risk through food chain arises from spreading sewage sludge directly on plants, in particular on those to be consumed raw or semi-cooked.

III.4.4.4.4. Hazard to animals

Both soil organisms and grazing animals are exposed to the xenobiotics in sludge-amended soil through soil and sludge ingestion. These highly bioaccumulative compounds accumulate in their tissues and are transferred through the food chain.

III.4.4.4.5. Hazard to humans

Human exposure to sludge-borne contaminants occurs through the food chain, due to consumption of animal products. Quantification of organic pollutants entering the food chain through this route has not been done yet. In the case of animal products – human part of food chain, the proportion of sludge-borne xenobiotics in the total diet and accumulation is difficult to evaluate, but considered low due to limited proportion of agricultural land amended with sludge for a longer time.

III.4.4.4.6. Monitoring requirements

Though extensive efforts on harmonization of sampling and analysis methods for organic pollutants in sludge and soil have been undertaken in the last 5 years in the EU level within the works on standardization for all the major groups of pollutants, i.e. heavy metals, organic compounds and pathogens, there are still no generally accepted and validated methods for analysis of most organic pollutants and for monitoring these compounds in sewage sludge and sludge-amended soils on the regular basis. Existing databases are limited and unevenly distributed, which is revealed in Table III.4.3. To the great extent, this situation is due to the lack of limit values for organic pollutants in the Sewage Sludge Directive 86/278/EEC (1986) in force, which were set just lately by the Working document on sludge (EC DG ENV, 2000) (Table III.4.3). The formulated urgent needs comprise (Langenkamp et al., 2001a): (i) elaborating the Priority list of organic contaminants based on key substances instead of substance classes as long as there are no internationally recognized toxicity factors; (ii) conducting research on soil–plant and soil–water transfer in sites heavily amended with sewage sludge in the past to provide scientific basis for limit values for soil concentrations; (iii) elaborating standardized methods for sampling and analysis of sewage sludge and amended soil; (iv) performing a survey of organic pollutants in the EU sewage sludge to establish standardized EU databank. These needs are actually similar for every country intending to use extensively sewage sludge in agriculture.

The persistent bioaccumulative compounds of high toxicity such as PCDD/Fs, PCBs and PAHs should receive the highest attention. Though these xenobiotics are consequently declining in European soils due to restrictive source control, the situation worldwide might be different (US EPA, 2000a).

Following extensive liquid chromatography column clean-up of solvent extracts, high resolution gas chromatography–mass spectrometry (HRGC/HRMS) can be used to determine PCDD/F content in sludges and soils (Jones et al., 1995; Henkelmann et al., 1999). The HRGC/HRMS technique, though, is very expensive that might be a barrier for the survey of these compounds on a regular basis. Use of much simpler and cheaper bioassay/biomarker technique for bioanalysis offers an attractive and reliable alternative for screening sludges and soils for dioxin and unknown dioxin-like compounds (indicated by AOX parameter) in sewage sludge and sludge-amended soils. In the last decade, a battery of *in vitro* bioassays and ligand binding assays for screening dioxins and dioxin-like compounds in complex environmental mixtures with an adequate reliability and accuracy has been developed, to be generally used in two-step process for identification of the materials and sites of interest; the identified sites are then to be analyzed by HRGC/HRMS (US EPA, 2000b; Behnisch et al., 2001). In particular, EROD and EIA(DFI) bioassays have been used to study dioxin-like compounds in sewage sludge (Schwirzer et al., 1998; Engwall et al., 1999; Engwall and Hjelm, 2000).

More detailed information on the bioanalytical tools for monitoring the effect of chemicals in the environment is given in Chapter IV.4 of this book.

III.4.4.5. Pathogens

Sludge-borne pathogens (Table III.4.6) mainly occur on the soil surface or at shallow depth when sewage sludge has been plowed into the soil. Pathogen penetration in the soil profile, in general, correlates with soil hydraulic conductivity. Survival of pathogens depends on the numerous indirect factors that comprise soil and climatic parameters, contents of pathogens in sludge and amount of sludge applied. Direct factors are related to the biological characteristics of the pathogen. Depending on these factors, survival periods may vary from a few days to several years and are generally shorter when the sludge is spread on the soil surface rather than plowed into soil.

Transfer to groundwater through infiltration and surface water through run-off is of the similar significance as for organic pollutants. Survival on the plants is generally shorter than in the soil due to better exposure to climatic factors. Transmission routes to grazing animals and humans are similar to those of organic pollutants (ANDERSEN--SEDE, 2001).

Sludges treated according to the recommended advanced methods (Table III.4.7) will not present risk to human, animals or plant health. Sludges that may contain BSE agent should not be applied to land where animals have access. If sludge is treated by conventional methods, planting, grazing or harvesting should be delayed for the time period sufficient to reduce pathogen numbers indicated by number of *E. coli* by at least a 10^2 factor. The duration of these constraints depends upon the local climatic conditions that vary significantly. Another mean of avoiding the direct contact with pathogen is incorporating sludge deep into the soil, though it increases a period of survival (Carrington, 2001).

III.4.4.6. General conclusion

To conclude, land application of sewage sludge provides an attractive sink for an unwanted waste and allows utilizing valuable nutrients and organic matter. The occurrence in sewage sludge of high concentrations of potentially dangerous inorganic and organic contaminants, persistent in the environment or of insufficiently known long-term effect, has necessitated restrictions on the quality and quantity of sludge that may be applied to land. With respect to heavy metals, the highly restrictive science-based approach is indispensable in order to prevent toxic effects on plants and soil fauna and heavy metal accumulation in the food chain (McLaughlin et al., 2000). For heavy metals, risk assessment should consider bioavailability and its alteration over time. For these purposes, new methods and models for assessing bioavailability, which incorporate both chemical parameters influencing metal toxicity and biological response factors, and for predicting its long-term changes should be developed and adapted in regulatory programs. With respect to organic contaminants in sewage sludge, the integrated research for assessing relative importance of contaminant contribution from sludge to soil, their long-term transformations, toxic effect and transfer routes (including soil–plant and soil–water transfer) are required to provide the scientific basis for setting priority lists, limit values for sludge and soil concentrations and justified regulations for sustainable sewage sludge use in agriculture. The general monitoring and database for all kinds of pollutants of concern in sludge and sludge-amended soil based on harmonized standard methods and procedure should be established as a regulatory and validation tool.

III.4.5. Other sewage sludge applications in land

III.4.5.1. Forestry and silviculture

The term "forestry" is used with respect to the amenity forests or mature forest management, while "silviculture" refers to the intensive wood production. The purposes, agronomic benefits and environmental implications and hazards of sewage sludge use are similar to those occurring at its application in agriculture.

EC studies (ANDERSEN-SEDE, 2001) point out, besides general adverse effects connected with heavy metal, organic pollutants and pathogen enrichment on wild fauna and flora, also possibility of degradation of the upper layer of forest soil and the humus, alteration in ecosystem, disturbance of biodiversity in natural biotopes and nitrogen leaching to groundwater. For these reasons, use of sewage sludge in forestry in some countries (e.g. in France) is prohibited. A risk to humans through the food chain is considered to be low due to insignificant share of forest products in the human diet. More research on this issue was postulated.

The mass balance of nutrients and trace element fluxes for 2001/2002 period of 5-years' (1998–2003) field experiment with application of biosolids in the form of liquid and solid composted sewage sludge added at low annual rate 3 t/ha d.m. to podzol soils in 8-year-old maritime pine stands in France (Benbrahim et al., 2003) showed significant increase of nutrients in amended soil in particular Ca (by 23–240%) and N (by about 30%) but also enrichment of trace elements, in particular Zn (by 45–94%) and Cu (by 30–91%) compared to the background level. Pb and Ni increase was lower (by 2–8 and 3–18%, respectively), though for all trace elements it can be defined as high or very high (higher values were reported for composted sludge). The major part of the mineral elements was found to retain in the upper 0–20 cm humus soil layer and did not affect groundwater quality and metal concentrations in the understorey vegetation that showed 200% (liquid sludge) and 50% biomass increase and temporary growth of the species' number, while pine productivity increased by 10% at liquid sludge treatment. Liquid sludge application, though, was reported to significantly increase Pb concentrations in mushrooms and snails.

This example confirms (i) possibility of significant heavy metal enrichment in soils due to long-term application of sewage sludge (biosolids) even in low doses, similarly to that observed at prolonged use of sewage sludge in agriculture; this undermines optimistic prognosis derived on a 1-year basis regarding thousands of years required for metal accumulation in soil to reach a limit value; (ii) nonequivalence of total metal enrichment and its bioavailability (as it can be exemplified in Pb increase and no effect of high Zn and Cu enrichment in sludge-amended soil on uptake by snails, mushrooms and grass); (iii) difference in metal binding mechanisms and strength between sewage sludge and soils.

Vigorous development of understorey biomass and rather poor increase of pine productivity support the thesis about successful competition of weeds with high trees growth, especially in amenity forest. Consideration of protecting natural ecosystems and biodiversity, wild fauna and flora militates against wider use of sewage sludge, which is a remarkable harvester of all anthropogenic pollutants, in forestry and any other natural ecosystem. Sewage sludge use as soil amendment should be limited to plantations purposely cultivated for intensive wood or energy production under permanently controlled conditions. Application of sludge and wood–ash mixtures to energy forestry plantations (*Salix* sp.) has been found to be promising (Dimitrou et al., 2003).

III.4.5.2. Land reclamation and revegetation

Use of sewage sludge for land reclamation and revegetation aims to restore derelict land or protect soil from erosion through supporting humus layer and/or vegetation development. In many derelict post-industrial sites (e.g. after opencast mining, in waste dumping sites) topsoil is often absent and waste material is depleted of nutrients and is thus extremely unfriendly for purposeful plant introduction or natural plant invasion. Application of sewage sludge in such sites, often in mixture with other inexpensive or waste soil improvers has been reported to give positive results, e.g. use of sewage sludge and lime for reclamation of smelter waste pile (Stuczynski et al., 2003) or mixed biosolids for revegetation of fly ash and coal reject disposal site (Danker et al., 2003). Sewage sludge for derelict land reclamation has been already performed in Sweden, Finland, Germany and the UK (ANDERSEN-SEDE, 2001).

It is assumed that the risks in this case are lower than in the case of sewage sludge land spreading for agricultural production or in forestry, as these lands are not considered for food production, and no natural ecosystems are impacted. In the case of erosion control though, these concerns exist, in particular at sewage sludge (biosolids) application to sloping land that enhances pollutants transfer through run-off.

III.4.6. Incineration and alternative technologies

III.4.6.1. Incineration

Sewage sludge incineration with energy recovery seems to be an environmentally safer way of sewage sludge utilization provided that point ("end-of-a-pipe") emissions to air, soil and water from this process are adequately controlled. This alternative prevents the hazard of non-point contamination of the terrestrial and aquatic environment that occurs in agricultural application of sewage sludge through spreading contaminants in vast areas, in particular that there are still wide gaps in knowledge concerning long-term pollutants routes, fate in the terrestrial and aquatic environment and toxic impact.

The rationale behind thermal waste treatment is discussed in detail in Chapter VI.3 focused on municipal waste but thoroughly applicable to sewage sludge.

Different techniques of incineration are currently in use, including sewage sludge and municipal wastes incineration in dedicated incinerators, or co-incineration, e.g. with coal in power plants for energy production. In this case, emissions into the air of chlorinated aromatics as PCDD/Fs, besides other common products of combustion, are of particular concern (Samaras et al., 1999, 2000, 2001). Modern incinerators assure environmentally safe levels of emission; recent research shows possibility of significant increase of cost efficiency of PCDD/F elimination in flue gases from co-combustion through use low-cost additives to the input. Solid waste from combustion process is another emission source that is environmentally problematic: much lesser volume of this waste product makes it easier to manage in an environmentally safe way.

III.4.6.2. Alternative technologies

Besides conventional combustion or co-combustion processes, several novel alternative technologies are being introduced onto the market, e.g. pyrolysis, gasification, wet oxidation or combination of these processes. These technologies offer advantageous solutions with respect to cost efficiency and the environmental impact. One of such lesser known but fully implemented technologies is presented in Figure III.4.4.

PYRO-KAT Technology of sludge mineralization (Rydzewski and Golos, 2002) comprises water evaporation unit (both for primary dewatered or non-dewatered sludge); water vapor sanitation unit; system for low-temperature processing of organic matter present in sludge; catalytic reactor for oxidizing organic matter to H_2O and CO_2 with 99.9% efficiency; heat exchanger system for energy utilization; filters for uptake of solid residues (including metals and metal compounds).

The advantages of the technology are: (i) lack of combustion chamber: process is conducted in temperature $\leq 500°C$ that greatly reduces energy demand; (ii) complete oxidation of organic matter to H_2O and CO_2; (iii) mineral residue accounts for 2–4% by mass of the initial input; (iv) low operational costs; installation comprises heat recovery system in catalytic reactor that is reused in the process.

Lack of hazardous emissions into the air, including PCDD/F, and low energy demands are claimed to be the most advantageous characteristics of this technology.

III.4.7. Other emerging sludge applications

III.4.7.1. Contaminated site remediation

High enrichment of heavy metals and organic pollutants in sewage sludges results from their high, though variable, sorption properties for these pollutants. CEC for 60 sludges

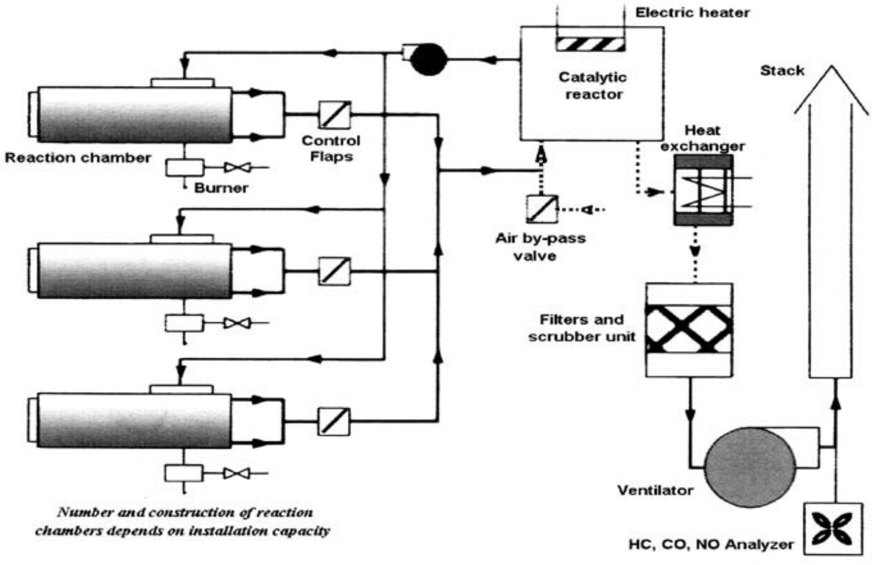


Figure III.4.4. Technological scheme of sewage sludge mineralization process (PYRO-KAT) (Hendri-Gras Chemicals B.V.).

was found to range from >10 to >100, at pH acid to neutral; the sorption capacity of sewage sludges might be up to 10 times as high as that of soils (Siebielec et al., 2003). Sorption sites in sewage sludge, in general, are not fully occupied. This has given rise to the idea of using these properties of sewage sludge for decontamination of metal contaminated sites (Brown, 1997; Li et al., 2000; Siebielec et al., 2003). The major concept is soil remediation by stabilization, i.e. by reducing the mobility of heavy metals through the addition of sewage sludge rich in organic matter. The significant difference in sorption capacity for metals has been explained by difference in humic acid (HA)/fulvic acid (FA) ratio (Shuman, 1999), though most probably it is not the only reason, and binding onto inorganic sites should be equally regarded. The affinity of metals and As to sorption onto organic-rich waste was reported to follow the order Pb $>$ Cd $\geq$ Cu $>$ Mn $\geq$ Zn $>$ As, though formation of soluble metal-organic chelates partly counteracted the sorption effect (Madejon et al., 2003). This opposite effect can be used to enhance phytoremediation. Propensity to mobilization and/or immobilization of metals from sludge-amended soils is known to be strongly affected by soil factors (Brown, 1997; Miner et al., 1997), thus soil quality parameters, which are often extreme and subject to alteration over time in industrial contaminated sites, should be considered at the designing remediation program with use of sewage sludge as metal binding and mobilizing agent. For this purpose, more research is needed to explain and purposely control mechanisms of soil–sewage sludge interaction. The overall idea of using sewage sludge for decontamination of contaminated sites is attractive, cost effective and the least controversial, provided that it is properly applied.

III.4.7.2. Using as a sorbent in small commercial premises

Analysis of contaminant sources and source control status that might have influence on sewage sludge quality with respect to the environmental hazards have shown that while large industries achieved required improvement in this field, in the countries where adequate regulations and their implementation exist, small manufacturing industries (e.g. metal electroplating and vehicle related activities, laundries, etc.) still contribute significantly to the contaminant load in UWW. These enterprises usually cannot sustain economically application of advanced technologies of contaminant removal; their small scale also often reduces their feasibility.

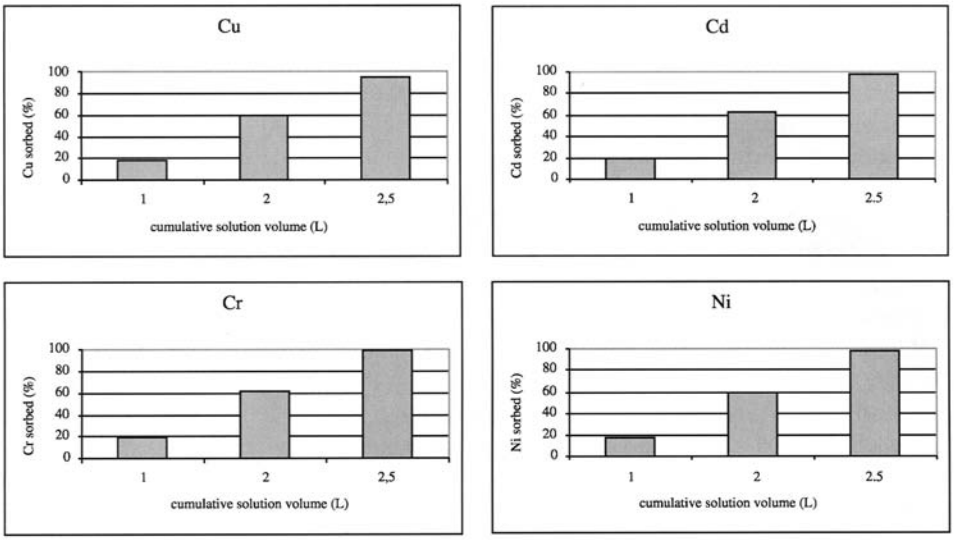
Experiments with metal sorption from electroplating effluents with use of sewage sludge in a simple batch reactor (a tank with mixing device) have shown high efficiency and feasibility of this process that can be exemplified in Figure III.4.5 (Avnimelech and Twardowska, 1997). Therefore, use of small amounts of sewage sludge as adsorbent that after use should be further directed to incineration, could greatly and practically at almost no cost improve quality of bulk sewage sludge to enable its environmentally sustainable use in agriculture. Further experiments in this promising field of application, also with the use of sewage sludge as adsorbent for organic pollutants are needed.

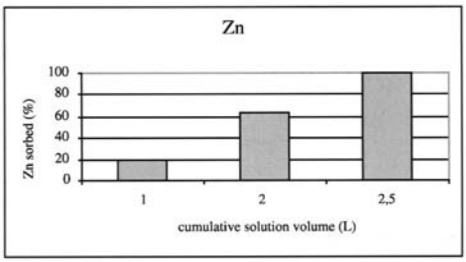
III.4.8. Landfilling

Landfilling of sewage sludge that can be performed as mono-disposal of sewage sludge only (usually at WWTP landfills) or as commonly used co-disposal with municipal wastes is the least advanced technology of utilization of this waste. The landfill construction and emissions from landfill operations are of commonly known character adequately presented in guidelines, and are not addressed in this chapter. Since landfill sites are primarily intended for dumping of municipal solid waste, much opposition exists concerning their use for the disposal of sludge.

When sewage sludge is to be landfilled, its volume needs to be reduced as much as possible. To accomplish this, the sludge must be dewatered, dried, incinerated or undergo wet oxidation. Dewatering avoids the addition of a large amount of water into the landfill body and also reduces adhesion of sludge to the tires of transport vehicles and compactors. Thermal drying can increase the dry solids content by up to 90%. This reduces transportation costs and effectively meets dumping requirements. The dried sludge needs to be pelletized before being dumped, to avoid dusting. Once the pellets are dumped, there is a delay before they take up water from the landfill. When they are moist enough, the pellets will become involved in the microbiological process of the landfill body and leachability will increase with time (Van den Berg, 1993).

Co-disposal of domestic waste and sewage sludge increases the stabilization of the wastes. The reduction of degradable organic compounds leached from the waste is then more rapid and eventually, the quality of the leachate improves. On average, it has been found that the concentrations of heavy metals in leachates from landfills without sludge are higher than in leachates from landfill sites used for co-disposal. This finding was unexpected, as the total metal content in the co-disposal landfill site is greater than in the





Examples of removal efficiency (pilot scale, batch reactor 120 L, 1:10 ratio, single treatment cycle)

METALS	Zn	Cr	Cu	Cd	Ni
Electroplating waste I					
C_{input} mg/L	163.0	193.0	172.0	53.40	14.90
C_{output} mg/L	27.1	9.0	16.8	3.86	1.92
Reduction, %	**83.4**	**95.3**	**90.2**	**92.8**	**87.1**
Electroplating waste II					
C_{input} mg/L	121.6	10.4	19.0	4.75	3.39
C_{output} mg/L	13.9	3.6	10.0	0.30	1.30
Reduction, %	**88.6**	**65.4**	**47.4**	**93.7**	**61.7**

Figure III.4.5. Cumulative metal binding from electroplating waste onto stabilized sewage sludge in batch reactor in three subsequent sorption/desorption cycles with metals recovery (after Avnimelech and Twardowska, 1997). C_{input}, input metal concentration in treated liquid waste; C_{output}, metal concentration in outflow from the reactor. Sorption cycle: sludge:liquid waste ratio 1:10; desorption: 15% HCl; neutralization: $Ca(OH)_2$. Proven feasibility of repeated using the same sewage sludge as a sorbent. Efficiency of metal reduction: 50–95% (higher for high input concentrations, lower for low input concentrations due to lower concentration gradient between the initial content of a metal in sludge and waste).

landfill without sludge. This condition can likely be attributed to the lower pH of the moisture in the landfill without sludge (Van den Berg, 1993).

Landfill costs continue to increase as regulations have been tightening, in part due to the frequent public opposition to the siting of new landfills (Bierman and Rosen, 1994). Landfill operators demand higher solids content and suitable shear stress characteristics as conditions for tipping. These requirements have an impact on the sludge conditioning technology where sludge is disposed of in landfills.

The regulation sheet on landfills, issued by the work group "Waste" of the German Federal States, demands a minimum dry solids (DS) content of 35% for the unlimited incorporation of dewatered sludge from municipal sewage plants. The land must also be solid, capable of being driven over, and meet esthetic, hygienic and odor emission criteria (Thomas et al., 1993).

III.4.9. Concluding remarks

In view of fast growing amount of sewage sludge generation in Europe and worldwide, its use in agriculture as a source of nutrients and valuable organic matter appears to be the most attractive and cost effective, but at the same time also the most controversial disposal outlet due to exceptional concentration of heavy metals, metalloids and hazardous organic pollutants originating from all kinds of human activity and potentially high risk of non-point persistent contamination of vast areas of a vital importance for the environment and human health. It is well known that once occurs, non-point contamination is extremely difficult to reduce and control. To avoid risks, actual status of pollutants (metals and organics) occurrence, proportion of sewage sludge (biosolids) input to soil in overall mass balance from different sources, transfer routes and fate in the environmental media and food chain, reliable science-based long-term prediction of accumulation, distribution and redistribution among pools of different bioavailability, quantitative and qualitative transformations, as well as their direct and indirect impacts on organisms should be evaluated and documented. Short- and long-term predictive models and assessments need to be validated on the basis of permanent monitoring of heavy metals and organic pollutants level in sewage sludge and sludge-amended soil in parallel with sludge and soil factors influencing pollutants availability and toxicity based on standard sampling protocol and analytical methods.

With respect to metals, new regulatory programs that incorporate chemical speciation and species-specific bioavailability and reliable methods for its assessing, supported with relevant research programs, need to be developed. With respect to organic compounds, among many needs, harmonized priority list of pollutants based on the background information on input level and transfer routes, as well as long-term observations of the fate of organic contaminants and their metabolites for evaluation of persistence and toxic effects are required to develop reliable soil protection rates and quality standards.

The current development of solid science revealed the gaps in knowledge and amount of work to be done to mend them for safe use of sewage sludge (biosolids) for land spreading. This suggests preference of the precautionary approach to intensification of sewage sludge application in agriculture until the required level of knowledge is achieved.

In this case, incineration of sewage sludge in accordance with the best available technologies or new medium-temperature treatment technologies validated with respect to safe level of emissions to air may have to be applied.

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For further information

Continuously updated additional information is available on Web sites: http://europa/eu.int/comm/environment/waste/sludge/; http://www.igpress.com/biocycle.htm.