5 Modelling the environmental fate in the terrestrial environment

In this Chapter, the environmental fate modelling approach for the terrestrial environment is presented. The description is generally divided into modelling of concentrations in terrestrial compartments distinguished by land uses and/or covers (such as agricultural soils; section 5.1) and modelling of contaminants in (terrestrial) plants (section 5.2).

5.1 Environmental fate modelling for different land covers

The WATSON model is primarily an exposure model with which impacts are assessed and valued. Modifying the definition given by van de Meent et al. (1996) and in line with Severinsen and Jager (1998) an exposure model is defined here more specifically as a model that describes the relationship between emissions and chemical quantities that living organisms are exposed to. Pure environmental fate models on the other hand describe the relationship between emissions and concentrations trying to quantitatively answer the question of 'how much of a substance ends up where?'. Thus, model development and set-up may require different subdivisions of the zones (cf. section 4.3) in terms of compartments distinguished and parameterisation of these compartments if one was to either develop a pure environmental fate model or an exposure model.

5.1.1 Compartments distinguished in the terrestrial environment

One may think of different criteria based on which the subdivision of the terrestrial environment can be performed. Before elaborating these criteria a short non-exhaustive overview about how the terrestrial environment is further subdivided into compartments by several existing multimedia models shall be given which builds to a large extent on the detailed description of models in section 3.1:

- a multimedia workshop organized by SETAC recommends to distinguish at least three soils of different land use/soil types (Cowan et al., 1995b). No more specific recommendations on what land uses or soil types to distinguish are made.
- EUSES and SimpleBox 2.0 distinguish between three terrestrial compartments: 'natural', 'agricultural' and 'industrial' (Brandes et al., 1996; European Commission, 1996a). Apart from their physical dimensions (i.e., mixing depths and area fractions), the only difference between these terrestrial compartments is whether they receive only inputs from air, additionally from sewage sludge or direct inputs, respectively. There is no differentiation in terms of processes taking place at varying rates (e.g., different erosion rates, infiltration capacities).
- similar to EUSES and SimpleBox 2.0, USES-LCA also distinguishes between the three terrestrial compartments stated above (Huijbregts, 1999). Furthermore, the terrestrial compartments are allowed to have different pH values in order to better account for variable solubility and, thus, the organic carbon-water partition coefficient (K_{OC}) of dissociating substances as well as hydrolysis rates in water, soil and sediments. It is stated, however, that no pH-dependency for metals is as yet considered.
- CalTOX version 4 (beta) does not (appear to) distinguish between different land uses (McKone and Enoch, 2002). However, it distinguishes between three soil layers: ground-surface soil, root-zone soil and the vadose-zone soil below the root zone. This distinction is also made by the multi-zonal multimedia model IMPACT 2002 (Pennington et al., 2005).
- similar to CalTOX, a multimedia model for the Great Lakes (CHEMGL) distinguishes between surface soil and the vadose zone, as well as ground water (Zhang et al., 2003).
- multi-zonal multimedia models usually do not distinguish between different soil compartments, for instance BETR North America (MacLeod et al., 2001; Woodfine et al., 2001), EVn BETR (Prevedouros et al., 2004), CHEMFRANCE (Devillers et al., 1995), the global model by Scheringer et al. (2000b), ChemCAN (Woodfine et al., 2002). Exceptions to this are the POPCYCLING-Baltic model (Wania et al., 2000) and Globo-POP (Wania, 2003) where the terrestrial environment is further subdivided into agricultural/cultivated and non-agricultural/non-cultivated land.
- if an urban environment is to be considered, Diamond et al. (2001) suggest to also include an organic film that coats impervious surfaces when modelling semi-volatile organic compounds. This is in line with McKone and Bennett (2003) to have a thin soil layer at the air-soil interface in order to properly consider volatilisation.

The following conclusions are drawn from this overview:

- a distinction of agricultural soils is necessary for the sake of human exposure assessment.
- soils of non-agricultural use should be included at least in order to have 100 % soil coverage.
- in principle, also natural vegetation should be included for the sake of the travelling of some (semi-) volatile substances (e.g., Bennett et al., 1998). This inclusion, however, should be realized especially in the air quality model domain (i.e., presently the WTM, cf. section 4.1) due to the exchanges taking place between air and plant material. Focusing on the media soil and water in the present work, the inclusion of plant compartments for environmental fate reasons is, therefore, left to future model developments. However, plants are also important with respect to human exposure assessment towards agricultural produce which will be dealt with in section 5.2 and Chapter 7.
- information on direct emissions to soils other than agricultural land which receive inputs for example via sewage sludge and pesticide application is rather scarce. Therefore, also the distinction of an urban/industrial soil will not be made for the sake of receiving direct inputs. Leachates from landfills are primarily considered emissions to ground water which cannot appropriately be modelled at present for even less information on ground water is available than for soils.
- the inclusion of an organic film on impervious areas (cf. Diamond et al., 2001) is considered too special for a larger scale environmental fate and exposure model.

As was discussed in section 3.2, substances to be assessed in the present work are non-radioactive, non-degradable and non-volatile trace elements. Due to these properties, the main loss mechanisms from the terrestrial environment are linked to advective transport processes by water (cf. Scudlark et al., 2005) including soil erosion. In contrast to POPs for whose environmental fate and human exposure the soil erosion process including overland flow is found to be less relevant (Fiedler et al., 2000), it is estimated that about 95 % of the heavy metals that are transported from land to the sea is particle-bound (Morgan and Stumm, 1999). Furthermore, the soil metal contents depends on the erodibility of the surface soil (Nriagu, 1978). Beside potential human exposure pathways for example via crops and animal products, thus, permeability (in line with Becker, 1995) and soil erosion which amongst others is a function of the land use or management (cf. the C-factor in the Universal Soil Loss Equation, USLE, e.g., Wischmeier and Smith (1978) and Renard et al. (1997)) will serve as the main criteria for the dif-

Table 5-1: Terrestrial compartments distinguished according to qualitative criteria; their area shares in the geographical scope of the model are also given (derived from data presented in section B.3)

Compartment	Area fraction[a] [%]	Human exposure	Permeability	Erosion potential
Arable land	29	Via crops, animals and their products	high	moderate to high
Pasture	13	Via animals and products	high	low to moderate
Semi-natural ecosystems	50	n/a	high	low to very moderate
Non-vegetated land	1.4	n/a	high	high
Impervious surfaces	1.2	n/a	n/a	n/a
Glaciers	0.9	n/a	n/a	n/a

a.The remainder of about 4 % are freshwater bodies.

ferentiation of the terrestrial environment into compartments. The resulting compartments and their qualitative features with respect to the distinction criteria are given in Table 5-1.

The real distribution of the compartments within each of the zones is not explicitly considered. Still, their distinction overcomes the critical effects of averaging their variable characteristics over large areas (similar to the 'semi-distributed' approach as suggested by Becker (1995) for large scale hydrological modelling).

As the environmental fate of hydrophobic organic pollutants is highly linked to the presence of lipophilic matter, some spatially-resolved multimedia models allow the organic carbon content to vary (e.g., Wania et al., 2000; MacLeod, 2002). For similar reasons, WATSON-Europe, furthermore, includes varying pH values for the different environmental compartments in the distinguished zones (cf. section B.5) in order to take one of the key parameters into account that influences the partitioning behaviour of trace elements and particularly of metals (Sauvé et al., 2000; Kabata-Pendias and Pendias, 2001; Sauvé 2002). The mobility of trace elements such as lead, copper and chromium in soils may also substantially depend on the presence of colloidal organic matter (e.g., Bergkvist et al., 1989). However, appreciable colloidal transport beside preferential transport in general (cf. section A.3.7) is expected only to occur under rather acidic conditions ('podzolation') for which the pH value is an indicator noting that the mobility of copper and lead may not depend so much on the pH (Bergkvist et al., 1989).

Information on land use, soil pH and organic carbon content as well as on hydrology are taken from several sources (Batjes, 1996; EROS Data Center et al., 2000; Hansen et al., 1998; New et al., 1999; European Environment Agency, 2000; Lehner and Döll, 2001; Döll et al., 2003; cf. sections B.3 and B.5).

For each of the compartments, both its dimension and the processes possibly taking place need to be defined which will be defined in the following.

5.1.2 Dimensions of the terrestrial compartments

The areas that the respective soil compartments cover are determined based on GIS datasets (cf. section B.3). Unfortunately, no such GIS dataset is available at justifiable costs for the soil depth which is especially needed for the volume calculations (cf. section A.4). Therefore, the soil depth needs to be defined in a different way.

In Table 5-2, the depth for natural soil, agricultural soil and unspecified land use is shown as assumed in some multimedia models. Note that models that purely base the soil depth on a Damkoehler number-derived effective penetration depth are not considered for the reasons given in section B.3.2.

Without considering the maximum allowable effective penetration depth of SimpleBox 2.0 (Brandes et al., 1996), the soil compartment depths range from 0.01-0.1, from 0.05-0.3 and from 0.1-0.3 m for natural, agricultural and unspecified soil, respectively.

Before deciding upon a soil depth the following arguments should be reflected:

- usually agricultural land is assumed to be ploughed. This, however, only applies to arable land. Furthermore, tillage practices show different degrees of soil reworking/disturbances. Only ploughing really homogenizes the top soil while being the most disturbing tillage practice leading to homogenized soil depth between 20 and up to 60 cm in vineyards (Schütte, 2003). Principally one can distinguish between no-inversion and inversion practices, a variant of the former being no-tillage. Thus, for no-inversion techniques principally no homogenisation takes place (as intended) and for the others the ploughing layer in central Europe is about 30 cm which is the case for instance on 60 % of the arable land in Germany (Schütte, 2003),

Table 5-2: Overview on different soil depths adopted by selected multimedia models

Soil type	Depth [m]	Reference	Remarks
Natural soil	0.01-1.0	SimpleBox 2.0 (Brandes et al., 1996)	one metre is an upper limit to the effective penetration depth
	0.05	EUSES (European Commission, 1996a)	
	0.1	POPCYCLING-Baltic model (Wania et al., 2000)	forest soil
	0.01-0.1	Wania and Mackay (1995)	soil not receiving direct input; variable values due to different zones
Agricultural soil	0.2-1.0	SimpleBox 2.0 (Brandes et al., 1996)	one metre is an upper limit to the effective penetration depth
	0.2	EUSES (European Commission, 1996a)	
	0.05-0.25	POPCYCLING-Baltic model (Wania et al., 2000)	agricultural soil; variable values due to different zones
	0.15-0.3	SoilFug (Barra et al., 2000)	values for different Uniform Geographic Units; not a fully integrated multimedia model
	0.1	Wania and Mackay (1995)	soil receiving direct input
Unspecified soils (i.e., no distinction made or no type of soil indicated)	0.15	CHEMFRANCE (Devillers et al., 1995)	
	0.1	Scheringer et al. (2000b)	
	0.2-0.3	SoilFug (Barra et al., 2000)	values for different sub-basins; not a fully integrated multimedia model

- other homogenizing processes that can in places even affect several decimetres include bioturbation (e.g., by ants, moles, earthworms, earthlings), cryoturbation (driven by the change of freezing and thawing water) and peloturbation (driven by wetting and drying of soils rich in clay, Scheffer and Schachtschabel, 1989). However, significant contributions are only expected on soils with good water, air and nutrient conditions, on soils in the tundra climate, and on soils with a high clay content and changing water contents, respectively. The available GIS datasets do not allow to distinguish these soil types appropriately. Furthermore, the delimitation of natural vs. agricultural soil does not follow any of the just stated environmental properties,
- Jury et al. (1990) have shown that volatile organic compounds that occur well below the air-soil interface would need to be buried by a soil cover several metres deep in order for some of them not to re-enter the atmosphere. This means that for the sake of reducing the potentially underestimated volatilisation of these substances a soil depth larger than 0.1 m for natural soil should be chosen,
- the organic carbon content and the pH of the soil are identified to be the two key properties which influence the mobility of organic compounds and of metals, respectively. These are considered by the environmental fate model implemented in WATSON. The best and most readily available GIS dataset on organic carbon contents and pH values of soils for the geographical scope of WATSON is provided by Batjes (1996) (see section B.5.1 on the processing of these information). Information are given for 0-30 cm and 30-100 cm. This suggests to consider a soil thickness of between 0 and 30 cm for the ease of data processing.

For WATSON, a uniform depth of 30 cm is adopted which is at the higher end of the so-far assumed soil compartment thicknesses given in Table 5-2. This is motivated by the circumstance that WATSON is an exposure model which is why deeper surface layers than the root zone are generally not of interest, apart from ground water that is not considered at present. Furthermore, the findings by Jury et al. (1990) stated above together with the data availability issue suggest to use a soil depth between 0.1 and 0.3 m. A third reason may be that except for the models by Wania and co-workers (e.g., Wania and Mackay, 1995; Wania et al., 2000), multi-zonal multimedia models usually do not allow the soil depths of different zones to vary (e.g., Devillers et al., 1995; Scheringer et al., 2000b). Note that this default depth only applies to pervious soils, i.e., arable land, pasture, semi-natural ecosystems and non-vegetated land. The compartment depths of glaciers and impervious land will be addressed below.

5.1.3 Definition of the phases of terrestrial compartments

To the knowledge of the author, there is no GIS dataset available on soil texture data from which to define the volume share of void spaces in soils. Furthermore, a water content needs to be additionally defined for example for the calculation of the equilibrium distribution coefficient (section A.2). There are two publications of a multi-zonal multimedia model where these parameters are assumed to vary (SoilFug, e.g., Barra et al., 2000 and the model described by Wania and Mackay (1995), see Table 5-3). Whereas in the model by Wania and Mackay the volume share varies between zones and land uses, the ranges of volume shares in SoilFug are 20-30 % for water and the reverse for air, always yielding 50 % void space. Similar values are used by McKone and Bennett (2003) whereas in SimpleBox 2.0 (Brandes et al., 1996) a rather sandy soil (according to void spaces) is assumed which is probably due to screening level risk assessment assumptions or might reflect the high end of properties found in Dutch soils.

Although soil texture and soil moisture will vary significantly in space and time, this is not taken into account due to lack of information. In order not to be too conservative, the volume fraction values used in SimpleBox 2.0 (Brandes et al., 1996) are not adopted. Instead, soils are assumed to have a loamy texture with 50 % void spaces. Assuming that the soils are at field capacity then means that 30 % of the volume consist of aqueous phase (water tension: pF = 2.5). One has to note, however, that for example in Spain there are areas affected by desertification for which this water content will be too high. On the other hand, wetlands are not treated as water bodies but (most likely) as natural soils having effectively no gas phase.

The volume fraction of solids in the impervious compartment is set to 1 vol.-% assuming that the surface itself does not act as an adsorbent. The glacier compartment is assumed to contain 5 vol.-% solids although no partitioning to them will take place due to the effective absence of liquid water.

Another parameter usually is held constant. This is the density of the solid phase. In multimedia models, assumed solid particle densities range from 2500 to 2600 kg/m^3 (see Table 5-3). Due to the fact that the organic carbon contents is allowed to vary within WATSON (cf. section B.5.1), the solid phase density will also vary to some extent. Since the mineral solid particles of soils usually are made up of quartz with a density of 2700 kg/m^3, a mean mineral solid density of 2650 kg/m^3 can be assumed (Scheffer and Schachtschabel, 1989) which is adopted in the present study. The organic solids are assumed to have a density of 1400 kg/m^3 (Scheffer and Schachtschabel, 1989) and consist of 50 weight-% organic carbon according to 'model' humic and fulvic acids as given by Schnitzer (1978). For impervious land uses, this value is set to 70 weight-% based on the consideration that the organic matter on roads mostly consists of soot which is richer in organic carbon (e.g., Gustafsson et al., 1997).

Table 5-3: Soil characteristics according to different multimedia models

Volume fraction			Mass fraction	ρ_{solid}	Reference	Comment
gas [-]	aqueous [-]	total void [-]	organic carbon [-]	[kg/m^3]		
0.2	0.3	0.5	0.02	2600	McKone and Bennett (2003)	
0.2-0.3	0.2-0.3	0.5	0.01-0.025	n/a	Barra et al. (2000)	coarse silty and coarse loamy soils
0.2	0.2	0.4	0.05	2500	Brandes et al. (1996)	rather sandy soils
n/a	n/a	n/a	0.03-0.05	n/a	Wania et al. (2000)	organic carbon content varies between zones
0.25-0.35	0.15-0.25	0.5	0.005 (polar)-0.02 (rest)	n/a	Wania and Mackay (1995)	natural soils; water contents: lowest in the subtropics and highest in the polar/boreal zones
0.30-0.40	0.15-0.25	0.55-0.60	0.005 (polar)-0.02 (rest)	n/a	Wania and Mackay (1995)	agricultural soils; water contents: lowest in the subtropics and highest in the polar/boreal zones; void space is highest in the tropics

5.1.4 Processes considered for the terrestrial compartments

There are different processes in the terrestrial environment implemented in existing multimedia models (Table 5-4). It is evident that the different models usually consider the same processes. The only exception is resuspension of soil particles in CalTOX (McKone, 1993b). The way the so-called process 'resuspension' is described in CalTOX it may be better termed 'wind soil erosion' due to the equilibration of particle-bound substances taking place within soils in the time between the deposition of these particles from and their resuspension into air. As a result, 'resuspension' as understood by CalTOX may have different meanings or implications (such as the substances or particles being inert) in contexts other than multimedia modelling. For the reasons why this process is not taken into account in the presented methodology refer to section 4.1.1.

Due to the effectively involatile nature of the considered trace elements, the diffusive processes will not be considered further. Furthermore, the same reasoning not to consider these processes applies as for wind soil erosion (cf. section 4.1.1). The question to what degree inactivation processes could or should be included in the environmental fate model is specifically addressed in section 4.2.3. Beside wind soil erosion, all the other advective processes as given in Table 5-4, i.e., water soil erosion, (saturated) overland flow (including interflow) and matrix leaching, are considered in the presented methodology. Their formulation is given in Table 5-5 and further discussed in separate sub-sections to A.3 also stated in the Table. Note that root uptake by plants which may constitute a further removal process from soils is part of section 5.2 and not described here.

5.1.5 Innovations as regards terrestrial compartments

There are several innovations introduced as regards the modelling of the terrestrial environment. These are

- pH-dependent partitioning,
- distinction of compartments other than natural and agricultural soils (in a spatially resolved context),
- the formulation of the soil erosion process, and
- the introduction of the preferential flow process.

These shall be presented in the following.

Table 5-4: Overview on different soil-related processes considered by selected multimedia models

Process	SimpleBox 2.0	CalTOX 3.0	POPCY-CLING-Baltic	SoilFug[a]	CHEM-FRANCE
Degradation/chemical transformation/inactivation					
overall	x	x[b]	x	x	x
Advection					
leaching/ infiltration	x	x	x[c]	(x)[d]	x
overland flow/runoff	x	x	x	x	x
erosion	x	x	x[e]	(x)[d]	x
resuspension of soil particles		x			
Diffusion					
volatilisation	x	x	x[f]	x	x
deposition of gases	x	x			x
Reference	Brandes et al. (1996)	McKone (1993b)[g]	Wania et al. (2000)	Di Guardo et al. (1994)	Devillers et al. (1995)

a. Mainly soil considered (no air compartment).

b. Although not treated separately, it is stated by McKone (1993b) that the overall degradation constant should reflect the rates of photolysis, hydrolysis, oxidation and reduction, and microbial transformation.

c. Together with runoff.

d. Probably together with runoff.

e. Only attached to particulate organic matter.

f. Modified two-resistance model.

g. Latest published documentation of CalTOX according to McKone (2003).

Table 5-5: Process formulations for terrestrial compartments as used in the present assessment

Name	Compartments involved[a]	Refer to section ... for more details	Formulation[b]	
Degradation	i = u, b, n, p, ag	A.3.1 (p. 395)	$k_{i,\ \text{deg}}(p, i, z) = A(z) \cdot fr\_\text{A}(i, z) \cdot d(i, z) \cdot \frac{\ln(2)}{t_{1/2}(p, i)}$	(5-1)
Radioactive decay	i = u, b, n, p, ag, gl	A.3.2 (p. 395)	$k_{i,\ \text{decay}}(p, i, z) = A(z) \cdot fr\_\text{A}(i, z) \cdot d(i, z) \cdot \frac{\ln(2)}{t_{1/2}(p, i)}$	(5-2)
Water soil erosion	i = b, n, p, ag	A.3.3 (p. 396)	$k_{i\text{-}w,\ \text{erosion}}(z, i) = A(z) \cdot fr\_\text{A}(i, z) \cdot v_{\text{erosion}}(i)$	(5-3)
Overland flow	i = b, n, p, ag	A.3.4 (p. 398)	$k_{i\text{-}w,\ \text{overland flow},\ pH\|C_{\text{org}}}(p, i, z) = \text{A}(z) \cdot fr\_A(i, z) \cdot \frac{v_{\text{runoff}}(z) \cdot fr\_\text{v}_{\text{quick flow/runoff}}(z)}{ED_{\text{bulk/aqueous}\ ,\ pH\|C_{\text{org}}}(p, i, z)}$	(5-4)
	u	A.3.4 (p. 398)	$k_{u\quad w,\ \text{overland flow, pH}\|\ C_{\text{org}}}(p, u, z) = \text{A}(z) \cdot fr\_A(u, z) \cdot \frac{v_{\text{runoff}}(z)}{ED_{\text{bulk/aqueous, pH}\|C_{\text{org}}}(p, u, z)}$	(5-5)
Ice melt	gl	A.3.5 (p. 400)	$k_{gl\text{-}w,\ \text{ice melt}}(z, gl) = A(z) \cdot fr\_\text{A}(gl, z) \cdot \frac{d(gl, z)}{t_{\text{residence}}(gl)}$	(5-6)

Table 5-5: Process formulations for terrestrial compartments as used in the present assessment

Name	Compartments involved[a]	Refer to section ... for more details	Formulation[b]	
Matrix leaching	i = b, n, p, ag	A.3.6 (p. 401)	$k_{i\text{-}gw,\ \mathrm{leaching,\ pH}\vert\mathrm{C_{org}}}(z,i,p) = A(z)\cdot fr\_\mathrm{A}(i,z)\cdot\dfrac{(1-fr\_v_{\mathrm{quick\ flow/runoff}}(z))\cdot v_{\mathrm{runoff}}(z)}{ED_{\mathrm{bulk/aqueous,\ pH}\vert\mathrm{C_{org}}}(p,i,z)}$	(5-7)
Reduced matrix leaching due to preferential flow	i = b, n, p, ag	A.3.7 (p. 402)	$k_{i\text{-}gw,\ \mathrm{pref\ flow,\ pH}\vert\mathrm{C_{org}}}(z,i,p) = -A(z)\cdot fr\_\mathrm{A}(i,z)\cdot\dfrac{v_{\mathrm{rain}}(z)\cdot fr\_v_{\mathrm{pref\ flow/rain}}(z)}{ED_{\mathrm{bulk/aqueous,\ pH}\vert\mathrm{C_{org}}}(p,i,z)}$	(5-8)
Preferential transport	i = b, n, p, ag	A.3.7 (p. 402)	$k_{i\text{-}gw,\ \mathrm{preferential\ transport}}(z,i,p) = A(z)\cdot fr\_\mathrm{A}(i,z)\cdot r_{\mathrm{preferential\ transport}}(p,i)$	(5-9)

[a] *ag*: arable (or agricultural) land; *b*: (bare or) non-vegetated land; *gl*: glacier; *n*: (semi-) natural ecosystems; *p*: pasture/grassland; *u*: impervious surface (urban/built-up area)

[b] *A*: area of the zone [m^2]; *d*: depth of a compartment [m]; *ED*: equilibrium distribution coefficient [-]; *fr_A*: area fraction of a compartment within a zone [-]; *fr_v*: fraction of a process velocity [-]; *k*: process rate as used in the coefficient matrix [m^3/s]; *r*: process rate [1/s]; *t*: residence time or half life [s]; *v*: process velocity [m/s]; symbols in parentheses denote a parameter's dependency on the pollutant ('*p*'), the compartment (generic: '*i*' and specific: see footnote a) and/or the zone ('*z*')

pH-dependent partitioning

As discussed in section 5.1.1, WATSON takes one of the key parameters into account that influences the partitioning behaviour of the investigated trace elements. This is the pH value which is allowed to vary in space in the terrestrial environment (cf. section B.5.1 for the derivation of the respective values).

Distinction of terrestrial compartments other than natural and agricultural soils

According to the selection criteria as specified in Table 5-1, not only soils with natural vegetation and those subject to agricultural management may be distinguished as done by state-of-the-art multi-zonal multimedia models. Their influence on the exposure assessment part of the Impact Pathway Approach will be investigated in a scenario analysis in section 9.3.3.

Spatially variable water soil erosion intensities

It was also stated in section 5.1.1 that the soil erosion potential of the respective land uses are taken into account when distinguishing between compartments (cf. Table 5-1). Principally one needs to distinguish between different types of water soil erosion (e.g., sheet, rill, inter-rill, gully erosion, Shen and Julien, 1993; Morgan, 1999). However, models usually only try to estimate one to few types of erosion. For instance, the empirical Universal Soil Loss Equation (USLE, Wischmeier and Smith, 1978) or its revised version (RUSLE, Renard et al., 1997) have experienced a wide range of applications because of their simplicity (least data demanding, van der Knijff et al., 2000). They are used for on-site soil losses and have been developed for sheet and rill erosion (Wischmeier and Smith, 1978). Most erosion models are usually developed only for being applied to a certain site so that absolute values of these models at the regional scale are not reliable (van der Knijff et al., 2000). Erosion models for the regional scale itself that provide quantitative data are, however, lacking (Wickenkamp et al., 2000; Bach et al., 2001). Even simple models that only predict potential erosion rates require at least information on soil texture (Hennings, 1994), a soil property for which hardly any information is available in publicly available GIS datasets that would support regionally differentiated erosion assessments.

As indicated above, when assessing soil erosion from a soil or agricultural science perspective, usually only the loss at a given site is of interest which leads especially to a reduced soil fertility or production capacity (Morgan, 1999). As a consequence, very few of the erosion models predict how much of the soil arrives at adjacent areas or compartments. Attempts have been made to relate the results of the RUSLE to inputs into streams for example by means of the sediment delivery ratio concept (Umweltbundesamt, 1999). However, the RUSLE is still too data demanding at the regional scale and the sediment delivery ratio concept is highly questioned (Walling, 1983).

No transport of eroded soil from one terrestrial compartment to another is considered in WATSON for two reasons: (a) the compartments distinguished are assumed to be homogeneous implying that re-distribution of eroded soil within one compartment is irrelevant and (b) there is a lack of information about the situation of one compartment relative to another (cf. section 4.2.2). Rather, only the transport from the terrestrial environment into surface freshwater bodies is assessed. Zaslavsky (1979) quoted by Golubev (1982) estimated that only 10 % of the gross erosion is transported to the larger rivers, the remainder mostly being only re-distributed in the terrestrial environment (e.g., deposited on the lower parts of slopes). Walling (1983) estimates that only about 0.1 % to 38 % of the gross soil loss reach the rivers' outlets and are represented in the so-called sediment yield.

In order to allow for different erosion intensities on different soil compartments, the following approach is adopted. First, a value that is representative for European conditions is identified which corresponds to the one used by Brandes et al. (1996) and European Commission (1996a) (see section B.5.3 for the reasoning). Then, the crop management factor (C-factor) of the Universal Soil Loss Equation (USLE; Wischmeier and Smith, 1978; Renard et al., 1997) is made use of. Reported values are provided by Golubev (1982), Umweltbundesamt (1999) and Morgan (1999). The fairly simple C-factor subdivision by Golubev (1982) is followed here according to Table 5-6.

In order to maintain the overall erosion velocity as presented above, the following distribution scheme is employed:

$$\begin{aligned} v_{\text{erosion}} &= \sum_i v_{\text{erosion}}(i) \\ &= v_{\text{erosion}} \cdot \sum_i fr\_A_i \cdot Weight_{\text{erosion, i}} \cdot x \\ &= v_{\text{erosion}} \cdot x \cdot \sum_i fr\_A_i \cdot Weight_{\text{erosion, i}} \end{aligned} \tag{5-10}$$

where

fr_A : fraction of the zonal area with water soil erosion that consists of compartment i [-] (defined based on Table 5-1)

v_{erosion} : overall erosion velocity [m per s]

Table 5-6: Relative erodibility of different land covers according to Golubev (1982) and their assignment to compartments as used in this study

Golubev (1982)		This study	
Land cover	C-factor range	Compartment	Relative weights
Bare tilled soil	1.0	Arable land, Non-vegetated land	1.0
Soil under crops	1.0-0.1	n/a	n/a
Soil under virgin grass	0.1-0.01	Pasture	0.05
Soil under virgin forest	0.001-0.0001	Semi-natural ecosystems	0.0005

$v_{erosion}(i)$: erosion velocity of compartment *i* [m per s]

Weight : relative erodibility weights of compartment *i* [-] (defined in Table 5-6)

x : scaling factor for water soil erosion [-].

Solving for the scaling factor, values of 3.01 and 3.10 are obtained when distinguishing four or three soil compartments with soil erosion, respectively. The compartment-specific erosion velocity is derived according to:

$$v_{\mathrm{erosion}}(i) = v_{\mathrm{erosion}} \cdot Weight_{\mathrm{erosion,\,i}} \cdot x \qquad (5\text{-}11)$$

yielding the values as given in Table 5-7 which depend on the number of compartments distinguished in an environmental fate assessment.

Although noting that the erosion process is selective with respect to particles of different size (e.g., Walling, 1983), it is assumed here to affect the bulk soil even including pore waters. One may argue that the process 'overland flow' is responsible for the transport of pore waters. However, overland flow is perceived here to entrain that amount of a substance contained in soils that is in equilibrium with water that flows at the surface or near the surface ('interflow') as described in section A.3.4.

It is clear that the approach selected in order to allow for spatially variable erosion intensities is not appropriate in any situation. It is considered a justified first approximation as this distinction is in line with both the considerably lower crop management factor of the Universal Soil Loss Equation (USLE) for forest and pasture soils (e.g., Golubev, 1982; Morgan, 1999; Umweltbundesamt, 1999)

Table 5-7: Compartment-specific water soil erosion weights and velocities depending on the number of soil compartments distinguished which show the related process

Compartment	Four compartments with water soil erosion are distinguished		Three compartments with water soil erosion are distinguished	
	Overall erosion weights[a]	Specific erosion velocities [m/s]	Overall erosion weights[b]	Specific erosion velocities [m/s]
Arable land	3.01	$2.86 \cdot 10^{-12}$	3.10	$2.95 \cdot 10^{-12}$
Pasture	0.15	$1.43 \cdot 10^{-13}$	0.16	$1.47 \cdot 10^{-13}$
Semi-natural ecosystems	0.0015	$1.43 \cdot 10^{-15}$	0.0016	$1.47 \cdot 10^{-15}$
Non-vegetated land	3.01	$2.86 \cdot 10^{-12}$	n/a[c]	n/a[c]

a.Relative weights as given in Table 5-6 times 3.01.
b.Relative weights as given in Table 5-6 times 3.10.
c.Not distinguished.

as well as with existing forest soil models (e.g., Reinds et al., 1995). Allowing the water soil erosion rate only to vary by compartments is, furthermore, supported by the present paucity or rather absence of regional erosion estimates for the whole of Europe or modelling capabilities even at the regional scale (Bach et al., 2001). In any case, it is novel in the realm of multimedia models in which no differentiation of the erosion rate according to zones and/or compartments has been made so far.

Consideration of preferential flow in soils

One process that is responsible for example for the transport of pesticides from soil surfaces to the subsurface and even into ground water is 'preferential flow' (Beven, 1991; Gish and Shirmohammadi, 1991) or to be more specific 'preferential transport' (Helling and Gish, 1991; Luxmoore, 1991; Stagnitti et al., 1995; Schwarz and Kaupenjohann, 2000). When preferential transport occurs, it means that the contact time between the percolating water and the soil matrix (i.e., the solid phase) is so small that no equilibrium between substances contained in the water and the surfaces of the soil particles can be achieved. Thus, the soil cannot act as a purifying filter to the extent which is expected under regular leaching processes. The preferential flow process is more the rule than the exception (Flury, 1996) and may have different causes (Wittig et al., 1985; Helling and Gish, 1991; Steenhuis and Parlange, 1991; Schwarz and Kaupenjohann, 2000) including colloidal transport (Jarvis et al., 1999; Noack et al., 2000). It even also applies to atmospheric deposition in forests (Wittig et al., 1985; Chang and Matzner, 2000). Preferential transport is potentially very important especially for the removal of non-degradable trace elements from the rooting zone. In contrast to all of the existing multimedia models known to the author, this process has not yet been included in any of these models so far.

The inclusion of preferential flow into the assessment involves the consideration of the fact that the part of the precipitation that undergoes preferential flow is not available for ordinary matrix leaching (cf. Eq. (5-8) in Table 5-5). This also implies that this portion of the wet atmospheric deposition immediately bypasses the top soil layer, reducing the input to the soil compartment (cf. Eqs. (4-5) and (4-6) in Table 4-3) which only constitutes the upper part of soils (cf. section 5.1.2). Thirdly, the preferentially flowing water also displaces parts of the soil pore water which may also contain colloids (cf. Eq. (5-9) in Table 5-5).

In order to appropriately formulate these processes, it needs to be known (a) how much of the percolating water undergoes the process of preferential flow and (b) how much of the substance contained in soils is transported to the subsurfaces.

Since preferential flow is known to also occur in arid climates with little to no runoff formation, the amount of water preferentially flowing through soils is assessed based on precipitation rather than on runoff. Preferential flow was chosen to be 1 % of the rain rate by default unless the water balance suggested to use a different value (cf. section B.5.2).

Data on the displacement of trace elements in soils due to preferential transport could not be encountered. However, it is known that the amounts of pesticides lost due to this process normally lie in the range of smaller than 0.1 % and 1 % and may reach up to 5 % under worst case conditions (Flury, 1996). When also including colloidal transport, a value for the amount to bypass the top soil layers of 0.1 %, thus, appears to be a reasonable first (conservative) estimate. In order to convert this overall mass balance into a rate, the 0.1 % are assumed to apply to an annual mass balance meaning that 0.1 % of the annual amount of substances present in the soil reaches the subsurface by preferential transport. The respective rate is, thus, 0.001 per year. One has to note, however, that this rate may be substantially higher for non-degrading substances such as trace elements. However, different volatilisation and adsorption behaviours, for instance, play a role here so that the value is adopted for the time being for any substance until more specific information becomes available.

5.1.6 Arable land compartment

Arable land is characterized by the production of crops for food or feed supply purposes, a 'normal' permeability and a substantial soil erosion potential at least due to episodic bare or dead fallow periods. At present all agricultural land that is not pasture or grassland is considered arable land (cf. section B.3 and left part of Fig. 5-1). In particular with respect to the soil erosion potential there might principally be a need to distinguish areas on which annual crops are grown from those with perennial plants (like vine, olive trees, fruit trees), respectively. This distinction is, however, not made at present.

Processes that are covered by the presented methodology and affect the arable land compartment are: degradation (section A.3.1), radioactive decay (A.3.2), water soil erosion (A.3.3), overland flow (A.3.4), matrix leaching (A.3.6), preferential transport (A.3.7) and removal by plants with subsequent harvest (A.3.8). Their formulations are also given in Table 5-5.

5.1.7 Pasture compartment

The pasture compartment is characterized by a 'normal' permeability and a reduced soil erosion potential compared to arable land and non-vegetated land due to a permanent vegetation cover. Pastures are the compartments on which grazing and free-range animals are kept. The distribution of pastures is shown to the right of Fig. 5-1.

Processes that are covered by the presented methodology and affect the pasture compartment are: degradation (section A.3.1), radioactive decay (A.3.2), water soil erosion (A.3.3), overland flow (A.3.4), matrix leaching (A.3.6) and preferential transport (A.3.7). Their formulations are also given in Table 5-5.

5.1.8 (Semi-) natural ecosystem compartment

By 'semi-natural ecosystems', any land use that is neither (heavily) influenced by human management like agricultural land (sections 5.1.6 and 5.1.7) nor is characterized analogously to one of the other terrestrial compartments, i.e., non-vegetated land (5.1.9), glaciers (5.1.11) and impervious or anthropogenically sealed soils (5.1.10). As a result, this compartment is intended to pool all those land covers that make the terrestrial area complete, i.e., adding up to 100 % (cf. to left of Fig. 5-2). One has to note that this compartment also comprises forests which are to varying degrees managed as well which is why the term 'semi' is added to the name of this compartment.

The semi-natural ecosystem compartment is characterized by a 'normal' permeability and a substantially reduced soil erosion potential compared to arable land and non-vegetated land due to a permanent vegetation cover.

Processes that are covered by the presented methodology and affect the semi-natural ecosystem compartment are: degradation (section A.3.1), radioactive decay (A.3.2), water soil erosion (A.3.3), overland flow (A.3.4), matrix leaching (A.3.6) and preferential transport (A.3.7). Their formulations are also given in Table 5-5.

5.1.9 Non-vegetated land compartment

By 'non-vegetated land', all areas are meant on which no vegetation is present and which do not classify as either built-up areas, glaciers or aquatic areas (cf. sections 5.1.10, 5.1.11 and 6.1, respectively). Examples are rocks, open-cast mining areas, dump and construction sites (cf. section B.3). The distribution of non-vegetated land is shown to the right of Fig. 5-2.

Although this compartment is rather heterogeneous in terms of the permeability of the different land uses contained (e.g., consolidated rocks vs. non-vegetated sandy areas, cf. Tables B-2 and B-3), it is assumed to show a 'normal' permeability. Due to the non-vegetated nature, the soil erosion potential is considered substantial.

Processes that are covered by the presented methodology and affect the non-vegetated land compartment are: degradation (section A.3.1), radioactive decay (A.3.2), water soil erosion (A.3.3), overland flow (A.3.4), matrix leaching (A.3.6) and preferential transport (A.3.7). Their formulations are also given in Table 5-5.

5.1.10 Impervious surface compartment

By 'impervious surfaces', only man-made areas are addressed. Notions like 'built-up areas', 'sealed soils' and 'urban areas' are used synonymously in the present study although putting emphasis on different aspects.

Impervious surfaces are assumed to be fully impermeable. As a consequence, they accelerate the transport of those substances that are deposited on these areas to streams. As the resolution of the land use geo-datasets is at least 1 km^2 (cf. section B.3), not all built-up areas or areas that are sealed are included, most notably roads. It is, thus, assumed that when adding all urban areas as given by the geo-datasets this sum constitutes a lower bound estimate of the existing impermeable areas (cf. to the left of Fig. 5-3).

It is difficult to define a volume of a compartment that does not have a depth according to the assumption of impermeability. In order to still provide a depth which is needed for volume calculations (cf. section A.4), two assumptions are made:

1. no long-term retention exists within the impervious surface compartment, and
2. no removal of substances occurs except for flushing, i.e., advection by water, and chemical transformation.

These assumptions lead to a situation where there is no sewage treatment or where it exists a pipe network that allows separate conduits to drain rain water on the one hand and domestic and/or industrial wastewater on the other. In order to allow for rapid flushing without storage longer than a year, thus, the volume is set to the annual amount of rainfall which is derived by zone as described in section B.5.2.

As a result, processes that are covered by the presented methodology and affect the impervious surface compartment are: degradation (section A.3.1), radioactive decay (A.3.2) and overland flow in its strict sense (A.3.4). Their formulations are also given in Table 5-5.

Note that no organic film compartment coating impervious surfaces as described by Diamond et al. (2001) is included at present as stated above.

5.1.11 Glacier compartment

As the presence of lakes seem to have a significant influence on the overall residence time of substances (e.g., Klepper and den Hollander, 1999) and glaciers are nothing but large frozen water bodies, these are distinguished as separate compartments noting that their overall area fraction is rather small (cf. Table 5-1 and to the right of Fig. 5-3). As the albedo, i.e., the proportion of light reflected by a surface, of glaciers is rather high and except for photodegradation chemical reactions in the terrestrial/aquatic environment are restricted to the presence of liquid water it is assumed that no degradation of organic compounds occurs. Thus, the overall residence time in glaciers is simply a function of their melting rate for any kind of (non-radioactive) substances.

The depth of glaciers is assumed to be 200 m which corresponds to mountainous glaciers in the northern hemisphere outside the polar region (Baumgartner and Liebscher, 1990, Table 9.3).

The only processes that are covered by the presented methodology and affect the glacier compartment are: radioactive decay (section A.3.2) and ice melt (A.3.5). Their formulations are also given in Table 5-5.

Note that glaciers could also be considered as part of the aquatic environment. Due to the water being mostly solid, i.e., frozen, glaciers are classified here as a terrestrial compartment.

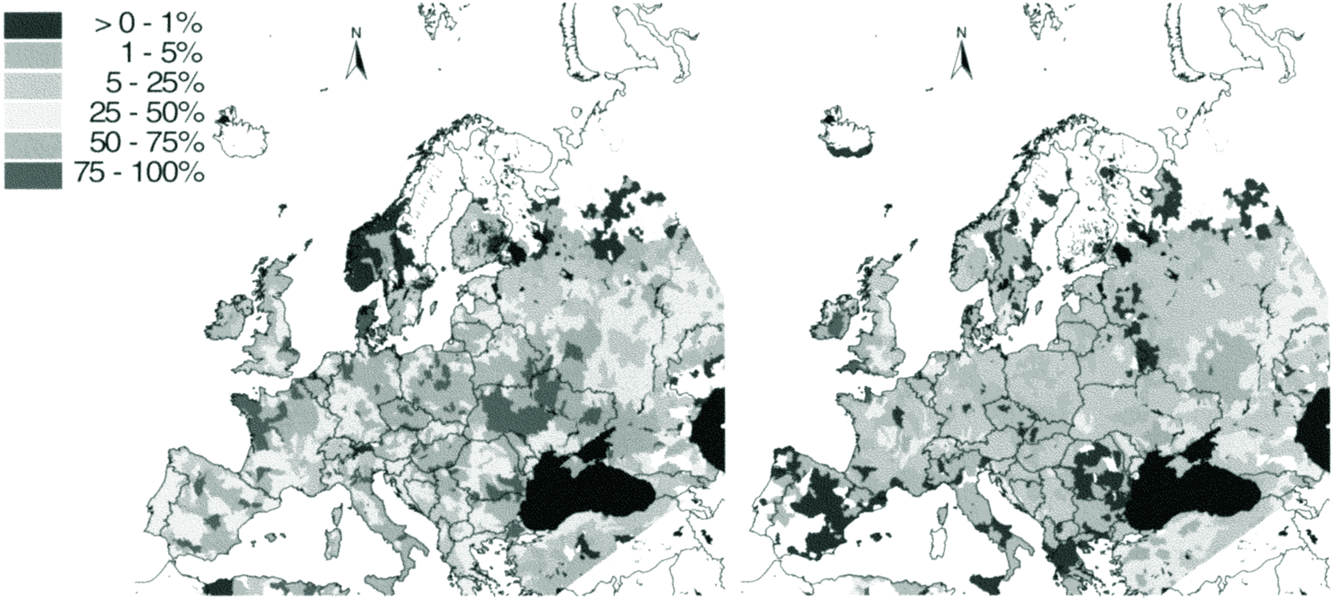

Fig. 5-1: Distribution of the predominance of arable land (left) and pastures/grasslands (right) in the different zones distinguished by WATSON

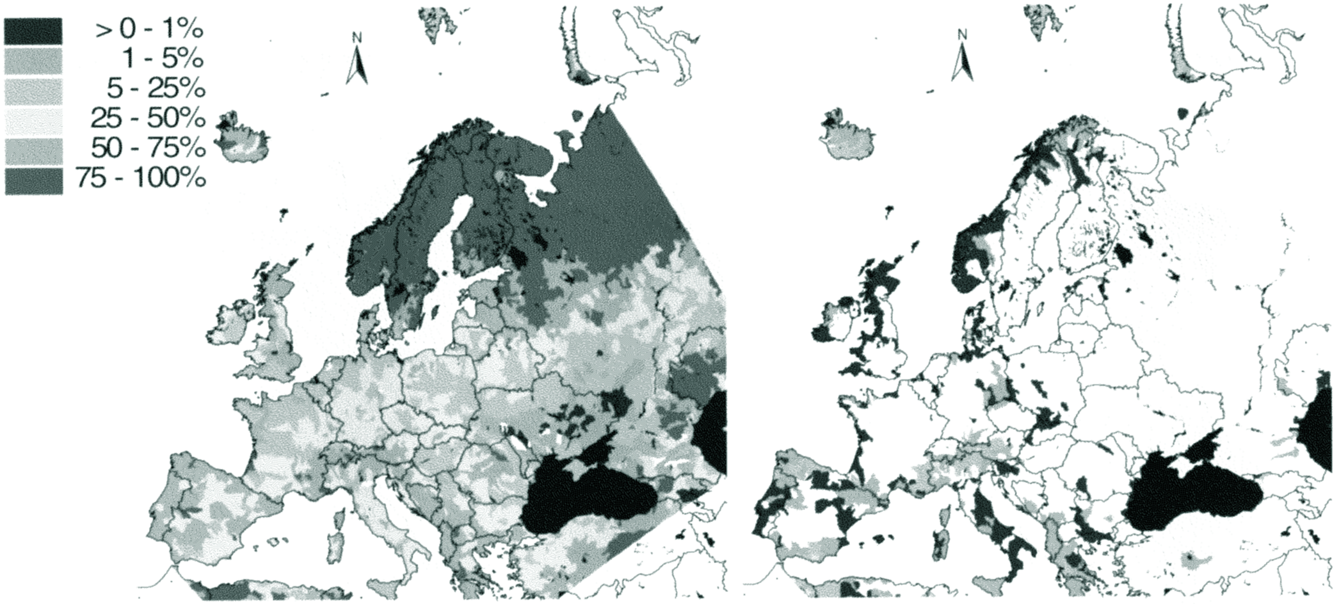

Fig. 5-2: Distribution of the predominance of (semi-) natural ecosystems (left) and non-vegetated land (right) in the different zones distinguished by WATSON

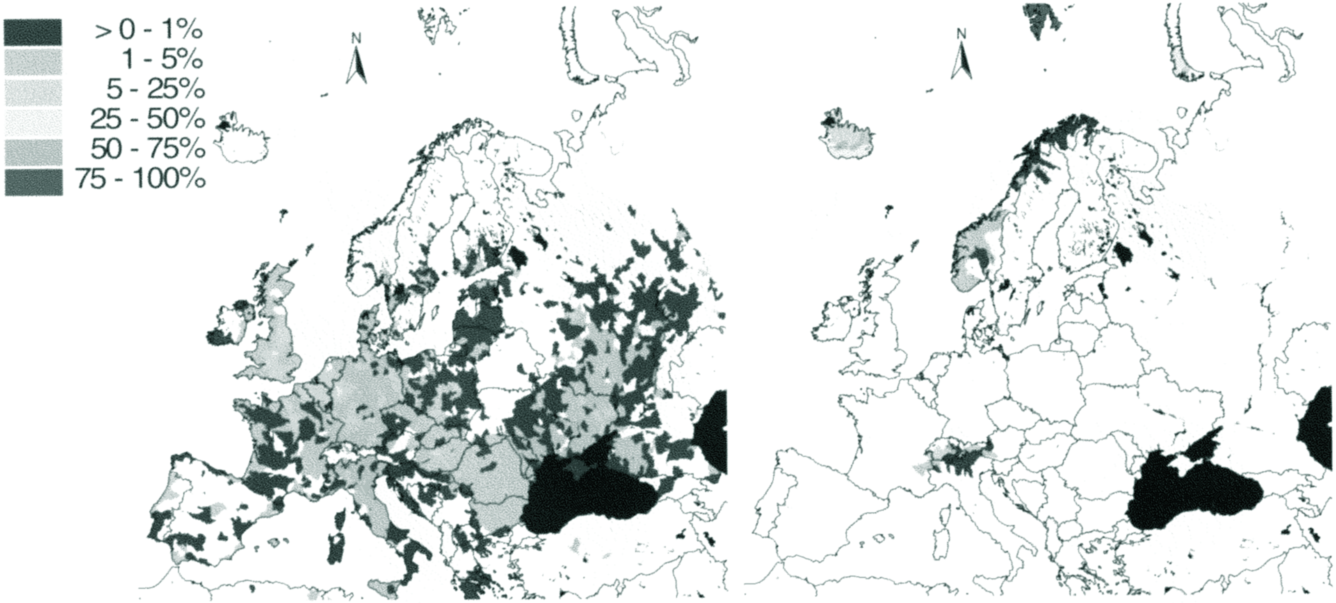

Fig. 5-3: Distribution of the predominance of impervious surfaces (left) and glaciers (right) in the different zones distinguished by WATSON

5.2 Environmental fate modelling for terrestrial plants

When assessing indirect human exposures, plants need to be considered since they form the basis of most of the food chains or webs due to their role as primary producers. How the inclusion of plants into the exposure assessment is realized, i.e., whether to include them only in the exposure part of the assessment or also in the environmental fate part or even doing without them, depends on two main factors:

1. in the case of (semi-) volatile compounds a vegetation compartment may influence the other compartments' concentrations (e.g., Severinsen and Jager, 1998) mostly sequestering these compounds (e.g., Simonich and Hites, 1994; Wagrowski and Hites, 1997) and, thus, reducing their atmospheric half-lives and consequently their characteristic travel distance (e.g., Bennett et al., 1998; McLachlan and Horstmann, 1998; Cousins and Mackay, 2001), and
2. some types of vegetation constitute food for humans or animals leading to exposure to substances entrained which for some substances dominates human exposure over inhalation (e.g., in the case of several semi-volatile organic chemicals, Bodnar et al., 2002). Apart from eastern Asian countries, aquatic plants rarely constitute a major contribution to the overall diet of the population. Therefore, only terrestrial plants will be treated in the following.

In case of 1), it is advisable to distinguish a plant compartment from soil compartment(s) if their characteristics of exchange with the air compartment are substantially different (Wania et al., 2000, as can be expressed by the filter factor, McLachlan and Horstmann, 1998). Cousins and Mackay (2001) recommend to include plant compartments into environmental fate models only when the substances are considerably taken up either via foliage or via roots. The criteria are formulated based on octanol-air and air-water partitioning coefficients. When introducing a plant compartment into an environmental fate model that is used for exposure assessments, care must be taken to make sure that this is done in a consistent way in order not to violate the mass conservation principle (cf. Hertwich et al., 2000).

When developing a concept for a plant model, the number of compartments to be considered needs to be determined. In the context of multimedia modelling frameworks, plant models of differing complexity are available. These range from single-compartment (e.g., Trapp and Matthies, 1995; McLachlan, 1996; Bennett et al., 1998; Severinsen and Jager, 1998), over two (e.g., Tolls and McLachlan, 1994), three (e.g., Paterson et al., 1994; United States - Environmental Protection Agency, 1998) to four compartment models (e.g., Trapp, 1995; United States - Environmental Protection Agency, 2002b; Charles and Jolliet, 2003). Most notably, spatially-resolved multimedia models usually only allow for one-compartment vegetation formulations (e.g., Wania et al., 2000; MacLeod et al., 2001) if at all (e.g., Scheringer and Wania, 2003). This is in line with the recommendation by Cousins and Mackay (2001) who suggest to have vegetation-soil pairs in order to allow for different vegetation types, each being represented by one aboveground compartment in addition to the soil compartment.

Reasons for distinguishing between several plant compartments either as different plant parts or as different plant species include:

- different plant parts are exposed due to different processes (especially foliar vs. root uptake, but also attachment of (particle-bound or gaseous) substances to plant aboveground surfaces),
- consumption occurs only of selected plant components (e.g., root, leafy, stem and corn produces),
- different plant parts or species are affected to different degrees by processes like harvesting, litter fall and growth, and/or
- if plants accumulate significant amounts on the expense of the amounts found/predicted in air and/or soil it is suggested to include them into multimedia models (Cousins and Mackay, 2001).

A non-exhaustive overview about existing plant models in the area of multimedia environmental fate and/or exposure modelling is given in Table 5-8. Of the models listed only two have been developed also for non-organic substances. These are United States - Environmental Protection Agency (1998) and TRIM.FaTE (United States - Environmental Protection Agency, 2002b). In the following, it will be tried to draw conclusions with respect to the different processes involved.

5.2.1 Exchange with air

Except for Reinds et al. (1995) and Trapp (2002), all models consider interactions between air and (aboveground) plants explicitly. Whereas some models assume that substances on leaves are in equilibrium with leaves (Bennett et al., 1998; Wania et al., 2000) which is debatable for some cases (e.g., due either to low cuticular permeability or to extremely low volatility and high lipophilicity of the assessed substances, Riederer, 1995) or neglect/disregard wet and/or particle-bound deposition (Paterson et al., 1994; Tolls and McLachlan, 1994; Trapp and Matthies, 1995; McLachlan, 1996; Severinsen and Jager, 1998), a few distinguish between substances in and on the leaves either as particulates (United States - Environmental Protection Agency, 2002b) or attached to the cuticle (Charles and Jolliet, 2003). United States - Environmental Protection Agency (1998) principally allows wet and dry deposition on (as well as gaseous exchange with) aboveground edible plant parts that are in immediate/intimate contact with air only (termed 'exposed produce' like leaf-vegetables, no cereals). As only the non-gaseous fraction of the chemical is allowed to undergo deposition, it can also be considered negligible for highly volatile substances. When fruits are distinguished they are not allowed to have direct exchange with air (Trapp, 1995).

The reason for excluding wet and/or particle-bound deposition onto plants by many of the models is that this process is only significant for low volatile, hydrophilic substances (Paterson et al., 1994; Trapp and Matthies, 1995). As a consequence this process cannot be neglected when having to deal with (weak) acids (many pesticides, e.g., Charles and Jolliet, 2003) and metals (e.g., Maddalena et al., 2002). Trapp and Schwartz (2000) state that it is unclear how to model particulate deposition because the chemical may remain sorbed to the particle after deposition (and washed off again), or it may migrate into the cuticle. In fact, there is some degree of contradiction whether leaf uptake is considerable for all or for some metals (Zimdahl and Koeppe, 1979; Ulrich, 1991; Weigert, 1991; Kabata-Pendias and Pendias, 1992; Greger, 1999). When not just allowing these deposits to stay on the surface but trying to define an exchange with the plant's interior, major problems in the process formulation occur (Riederer, 1995; and note in Maddalena et al., 2002). In case of TRIM.FaTE, the transfer rate needs to be provided by the user (Maddalena et al., 2002) which would require to provide hardly available values of another substance-specific parameter. Charles and Jolliet (2003) make use of an empirical relationship in order to derive a mobility rate based on a reference substance's mobility rate, a size selectivity of the cuticular membrane (which depends on the plant species) and the molar volume of the substance. They allow the exchange to occur over the full cuticle surface (expressed as the leaf area index (LAI) which is usually defined as the ratio of the area of the upper side of the leaves in a canopy projected onto a flat surface to the area of the surface under the canopy). This area appears to be too large as the deposits/residues will not cover the whole leaf surface.

It seems debatable whether to include an exchange between the deposits/ residues and the leaf interior. Bromilow and Chamberlain (1995) state that uptake through the cuticle mainly concerns non-polar organic substances with a log K_{OW} in the range from 1 to 3 whereas pesticides of which many are weak acids are not taken up as readily unless applied together with surfactants. On the other hand, exposure due to particles attached to leaf surfaces may play a role for non-volatile substances. It seems clear that there is a retention mechanism for some metals by leaves (e.g., for lead by forest leaves (Zöttl, 1985; Bergkvist et al., 1989; Lindberg, 1989; Rea et al., 2001) and additionally thallium (Weigert, 1991) and vanadium (Rea et al., 2001)). This may be due to the fact that the cuticular layer functions as a weak cation exchanger (Greger, 1999) which in turn would not in-

Table 5-8: Non-exhaustive overview on existing plant models in the field of multimedia models

Model reference	Number of plant species/types and components	Processes considered
Bennett et al. (1998)	1 plant species/type, 1 aboveground component	chemical-specific vegetation/air and soil/air partitioning; kinetics of mass transfer rates among air, vegetation and soil; degradation rates in air, plant tissue and soil; litterfall (equals growth rate); explicitly neglected: harvest
Charles and Jolliet (2003)	1 plant species/type, 4 components:	
	plant surface residue	diffusive exchange between leaf and plant surface residue; degradation
	foliage	diffusive exchange with air; diffusive exchange between leaf and plant surface residue; advective transfer to stem; advective transfer from stem (unclear whether included or not); degradation
	stem	active uptake from soil based on the transpiration stream concentration factor (TSCF); advective transfer from leaf (unclear whether included or not); advective transfer to leaf; degradation
	root	active uptake from soil based on the complementary of the transpiration stream concentration factor (TSCF); diffusive uptake from soil; diffusive transfer to soil;
Critical loads of heavy metals in soils (Reinds et al., 1995)	1 plant species/type, 1 aboveground component (growing forest parts)	growth uptake from soil (i.e., net uptake considering total root uptake, litterfall and canopy interactions, i.e., foliar uptake or foliar exudation) based on transpiration stream concentration factor (TSCF)

Table 5-8: Non-exhaustive overview on existing plant models in the field of multimedia models

Model reference	Number of plant species/types and components	Processes considered
McLachlan (1996)	1 plant species/type, 1 aboveground component (forage: grass/corn)	only air-plant partitioning considered for PCDD/Fs
Paterson et al. (1994)	1 plant species/type, 3 components (root, stem, foliage)	diffusion and bulk flow of chemical between soil and root; transport within the plant in the phloem and transpiration stream between root and stem as well as between stem and foliage; exchange between foliage and air and between soil and air; metabolism and growth; no harvest considered
POPCY-CLING-Baltic (Wania et al., 2000)	2 plant species/types, 1 aboveground component: coniferous forest needles and deciduous forest leaves	foliar uptake of gaseous substances; volatilisation; foliar uptake of dry particle-bound substances and substances contained in evaporating water droplets; seasonally variable dry particle deposition; seasonally variable volume due to growth; seasonally variable litterfall; metabolism; explicitly neglected: leaching
Severinsen and Jager (1998); SimpleBox 2.0 (Brandes et al., 1996)	1 plant species/type, 1 aboveground component	diffusive exchange between air and leaves via stomata; uptake from soil based on the transpiration stream concentration factor (TSCF); stomatal uptake of fine particle-bound substances; metabolism; harvest; death; explicitly neglected: cuticle uptake, wet deposition on leaves and foliage/stem-to-root transfer
Tolls and McLachlan (1994)	1 plant species/type, 2 aboveground components (leaf-surface, leaf-interior)	only diffusive exchange between air and leaf-surface as well as between surface and interior parts of the leaves

Table 5-8: Non-exhaustive overview on existing plant models in the field of multimedia models

Model reference	Number of plant species/types and components	Processes considered
Trapp (1995)	1 plant species/type, 4 components:	
	fruit	phloem flux from stem; metabolism
	foliage	transfer from stem with transpiration stream based on stem-foliage partitioning; phloem flux to stem; diffusive exchange with air; metabolism
	stem	active uptake from soil based on the transpiration stream concentration factor (TSCF); transfer to leaves with transpiration stream based on partitioning between stem and foliage; phloem flux to fruits; phloem flux from leaves; metabolism
	root	diffusive exchange between soil and roots in water and air pores ("probably realistic only for root cortex of intact roots ... upper limit for diffusive uptake into bulk root", p. 119); active uptake from soil based on the complementary of the TSCF; metabolism
Trapp (2002)	1 plant species/type; 1 belowground component (thick root)	active uptake without the help of the transpiration stream concentration factor (TSCF) or its complement; advective transfer to stem with transpiration stream; degradation; growth
Trapp and Matthies (1995)	1 plant species/type, 1 aboveground component (mainly foliage)	uptake from soil based on transpiration stream concentration factor (TSCF); gaseous deposition; volatilisation from leaves; transformation and degradation; growth; explicitly neglected: wet and particle-bound deposition

Table 5-8: Non-exhaustive overview on existing plant models in the field of multimedia models

Model reference	Number of plant species/types and components	Processes considered
TRIM.FaTE (United States - Environmental Protection Agency, 2002b)	1 plant species/type, 4 components:	
	particles on leaf	during rain: wet dry particle deposition from air; particles washed to soil; diffusive exchange between air and particles on leaf (note: not described by Maddalena et al., 2002) when no rain: dry particle deposition from air; particles re-entrained by air litter fall to soil or harvest if agricultural produce; diffusive exchange between leaf and particles on leaf; degradation
	leaf (interior)	diffusive exchange between leaf and air (note: only volatilisation but not absorption for mercury according to Maddalena et al., 2002) and between leaf and particles on leaf; litter fall to soil or harvest if agricultural produce; phloem flow to stem; xylem flow from stem; degradation
	stem	root uptake estimated by means of transpiration stream concentration factor (TSCF, in xylem) or the stem concentration factor (SCF, in bulk stem); stem to soil transfer; xylem flow to leaf; phloem flow from leaf; degradation
	root	root uptake estimated by means of root concentration factor (RCF) and a parameter describing the proportion of equilibrium value achieved; senescence (note: as mentioned in Maddalena et al., 2002); degradation

Table 5-8: Non-exhaustive overview on existing plant models in the field of multimedia models

Model reference	Number of plant species/types and components	Processes considered
United States - Environmental Protection Agency (1998)	3 plant species/types, 1 component each:	
	aboveground-exposed	direct deposition of particles; vapour transfer; root uptake based on plant-soil BCF (for organics according to Travis and Arms, 1988) for produce
	aboveground-protected	only root uptake based on plant-soil BCF (for organics according to Travis and Arms, 1988) for produce
	belowground	only root uptake based on root concentration factor (RCF; for organics according to Briggs et al., 1982), soil-water partitioning coefficient and empirical K_{ow}-dependent correction factor

fluence the environmental fate for instance of molybdenum (as molybdate), arsenic (as arsenite or asenate) and chromium (as chromium oxides). In fact, chromium does not seem to be enriched in forested ecosystems (Bergkvist et al., 1989). Unlike all other models, Severinsen and Jager (1998) allow stomatal uptake of fine particulates. However, this process does not lead to an accumulation on/in leaves that exceeds the pure deposition onto the soil and/or the leaves.

Overall, to what extent particle-bound substances will actually enter (Berrow and Burridge, 1991; Gawel et al., 2001) or just adhere to the leaves (Zimdahl and Koeppe, 1979), an issue that also depends on the metal (e.g., Bergkvist et al., 1989; Ulrich, 1991; Kabata-Pendias and Pendias, 1992; Greger, 1999; Rea et al., 2001; with contradicting evidence for lead), appears to be an unresolved question or at least one to which no generally applicable answer exists. It may, therefore, be concluded that gaseous air-leaf interactions can be neglected whereas particle deposition cannot for heavy metals that are predominantly transported in air in a particle-bound way. For gaseous mercury, the reverse conclusion applies.

The question remains to what degree the deposited metals will effectively be retained on or in the leaves[9] or even on other plant parts (e.g., the bark of trees, Schultz, 1987; Ulrich, 1991). Models apart from (measured) mass balances (e.g., Zöttl, 1985; Schultz, 1987; Lindberg, 1989; Rea et al., 2001) describing this retention are scarce. On the other hand, (heavy) metal retention by or temporary accumulation in aboveground plant parts that persist the next precipitation event may only be important if these plant parts are removed and enter the food chain as in the other case the metal amounts will be deposited to the ground due to litter fall.[10] For exposed produce, United States - Environmental Protection Agency (1998) allows for adhesion of wet deposition to the edible plant parts as well as an overall interception fraction comprising dry and wet deposition (cf. section A.6.5).

5.2.2 Exchange with soil

Principally, there are different approaches in order to model exchange processes taking place between plants and soils for organic substances and trace elements.

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[9] According to Riederer (1995), relatively polar ($K_{ow} \leq 10$) and involatile compounds accumulate almost exclusively in the aqueous phase (95 % for log $K_{aw} = -1$ and 100 % for log $K_{aw} \leq -3$).

[10] One has to keep in mind, however, that in case of natural vegetation and especially with coniferous trees litter does not occur annually if one wanted to allow for dynamic calculations which preferably should be done in annual time steps due to the hydrological data available.

Organic substances

Except for the works of McLachlan and co-workers, all models addressing organic substances consider chemical exchange between soil and plant. The uptake by aboveground plant parts via xylem flow is always based on the Transpiration Stream Concentration Factor (TSCF) and the transpiration stream flux with the exception of United States - Environmental Protection Agency (1998) assuming equilibrium conditions according to Travis and Arms (1988) whereas for Bennett et al. (1998) the modelling approach is unclear. Depending on whether more than one aboveground plant compartment is distinguished, the TSCF-derived stem concentration is further transported to leaves and/or fruits by advection and/or partitioning.

The treatment of roots widely differs between the modelling approaches. While some of the models do not (explicitly) treat roots (e.g., Reinds et al., 1995; Bennett et al., 1998), the other either (a) assume the (fine) roots to be in equilibrium with soil (without distinguishing a separate root compartment: e.g., Trapp and Matthies (1995) and Severinsen and Jager (1998); considering a separate root compartment with (Maddalena et al., 2002) or without basing the transfer on the Root Concentration Factor (RCF), United States - Environmental Protection Agency, 2002b), or (b) allow for kinetic exchange between root and soil (Paterson et al., 1994) sometimes based on the 'reflection coefficient' which is the complement of the TSCF ('1-TSCF', Trapp, 1995; Charles and Jolliet, 2003). United States - Environmental Protection Agency (1998) also assumes equilibrium by using the Root Concentration Factor (RCF), however, not integrated in an environmental fate model. Although TSCF is normalized to one (e.g., Bromilow and Chamberlain, 1995), the use of the reflection coefficient appears to be debatable. When deriving a mass balance for the root this coefficient may principally result (e.g., Trapp, 1995). However, if:

$$TSCF = \frac{C_{\text{xylem}}}{C_{\text{soil solution}}} \qquad (5\text{-}12)$$

then:

$$1 - TSCF = 1 - \frac{C_{\text{xylem}}}{C_{\text{soil solution}}} = \frac{C_{\text{soil solution}} - C_{\text{xylem}}}{C_{\text{soil solution}}} \qquad (5\text{-}13)$$

which is postulated to equal

$$1 - TSCF \equiv \frac{C_{\mathrm{root}}}{C_{\mathrm{soil\ solution}}} \cdot \alpha = RCF \cdot \alpha \tag{5-14}$$

where

TSCF : Transpiration Stream Concentration Factor [-]

C : C_{xylem}: concentration in the xylem [kg per m^3]

: $C_{\mathrm{soil\ solution}}$: concentration in soil solution [kg per m^3]

: C_{root}: concentration in the root [kg per m^3]

RCF : Root Concentration Factor relating root concentration to external solution concentration [-]

α : fraction of root concentration that is due to reflection of substances entrained in the (primary) transpiration stream [-].

This means that the following relationship is valid:

$$C_{\mathrm{soil\ solution}} - C_{\mathrm{xylem}} = C_{\mathrm{root}} \cdot \alpha . \tag{5-15}$$

It is fairly dubious to assume that concentrations add up although the TSCF may be considered to 'only' constitute a dimensionless relation factor and the respective volumes involved may be similar. Anyway, it is felt here that when employing an equilibrium coefficient like the TSCF for the stem's xylem concentration one should not use this measure in order to derive the concentration in the root. Rather, one should try to aim for consistency and employ the root concentration factor (RCF) which is a result of processes at equilibrium that are both diffusive and advective in nature. Moreover, modelling exercises for organic substances have shown that the diffusive exchange with the soil dominates root uptake (Trapp, 1995). This is supported by the observation that RCFs assume values well above 1 (e.g., Bromilow and Chamberlain, 1995) rendering the fraction of the root concentration α that is due to reflection to small values. Note, that for metals as opposed to lipophilic non-dissociating organic substances, higher concentrations in roots (although not in storage organs) than in soil have also been reported (Weaver et al., 1984; Speir et al., 1992). This might also be due to the fact that cell walls of roots (and potentially other plant tissue) act as cation exchangers, a functionality that is higher in dicotyledonous (like leguminous plants, trees) than in monocotyledonous plants (like grasses including cereals, Berrow and Burridge, 1991; Greger, 1999). As is discussed below, non-essential elements might be taken up as actively as essential elements due to similar physicochemical behaviours (see below). Another detoxifying mechanism might consist of chelate-forming organic molecules (such as phytochelatins or metallothioneins) transporting metals into vacuoles[11] followed by effective sequestration (Alloway et al., 1996; Mehra and Tripathi, 2000).

All models that treat roots explicitly allow for the process of non-advective exchange with soil. Trapp (2002) has developed a model for thicker roots that assumes that only the peel is in diffusive exchange with soil with respect to organic non-dissociating substances. However, the major part of the root consists of the root core into which only uptake with the transpiration stream is allowed. The model is reported to work fairly well for substances that have a log K_{ow} of less than 2 and that neither are polar nor constitute weak acids. For lipophilic substances, the model could predict concentrations in the peel well but gave unrealistically high concentrations in the core. Comparing the work by Trapp (2002) (Eq. (5-16)) with the approach proposed by United States - Environmental Protection Agency (1998) for belowground produce (Eq. (5-17)), shows that the models are similar when equilibrium situations are assumed (i.e., neglecting the growth and metabolism factor k in Trapp, 2002):

$$\begin{aligned} C\_w/v_{\text{roots}} &= \frac{Q_{\text{xylem}}}{\dfrac{Q_{\text{xylem}}}{K_{\text{rw}}} + k \cdot V_{\text{roots}}} \cdot C\_w/v_{\text{soil solution}} \\ &= \frac{\dfrac{Q_{\text{xylem}}}{K_{\text{sw}}}}{\dfrac{Q_{\text{xylem}}}{K_{\text{rw}}} + k \cdot V_{\text{roots}}} \cdot C\_w/v_{\text{soil solids}} \\ &\overset{\text{equilibrium}}{\Rightarrow} \frac{K_{\text{rw}}}{K_{\text{sw}}} \cdot C\_w/v_{\text{soil solids}} \end{aligned} \tag{5-16}$$

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[11] A vacuole is a membrane-enclosed fluid filled sac found in the cells of plants including fungi. A vacuole is often considered to be the plant equivalent of a lysosome in animal cells. From the point of view of its ability to break down large molecules under acid conditions, this is certainly the case. Furthermore, vacuoles have the facility to contribute to the rigidity of the plant; to cell elongation and to the processing and storage of waste products. Thus, it is generally assumed that vacuoles are temporary stores for reserve materials or final stores for waste products of the plant cell.

$$C\_w/w_{\text{roots}} = \frac{RCF \cdot Cor_{\text{roots}}}{K_{sw} \cdot \rho_{water}} \cdot C\_w/w_{\text{soil solids}} \tag{5-17}$$

where

C_w/x_{roots} : concentration in root on a weight by volume (x = v) or by mass (x = w) base [$kg_{\text{substance}}$ per m^3_{produce}] or [$kg_{\text{substance}}$ per kg_{produce}]

Q_{xylem} : transpiration stream flux [m^3 per day]

K_{rw} : partitioning coefficient between roots and soil water [l_{water} per kg_{produce}][12]

K_{sw} : partitioning coefficient between soil solid and aqueous phase [l_{water} per kg_{solid}]

k : removal rate coefficient due to growth and metabolism [day^{-1}]

V_{roots} : volume of roots [m^3]

C_w/v : concentration in soil aqueous (index 'soil solution') or solid phase (index 'soil solids') on a weight by volume base [$kg_{\text{substance}}$ per m^3_{soil}]

C_w/w : concentration in soil on a weight by weight base [$kg_{\text{substance}}$ per kg_{soil}]

RCF : Root Concentration Factor relating root concentration to external solution concentration [l_{water} per kg_{produce}]

ρ_{water} : density of water, i.e., 1 [kg per l]

Cor_{roots} : empirical correction factor that is 1 and 0.01 for substances with log K_{ow} less or greater than 4, respectively [-].

If RCF and K_{rw} can be considered equivalent, the main difference at steady-state is that United States - Environmental Protection Agency (1998) includes a correction factor in order to distinguish substances that are more lipophilic from those that are less, the log K_{ow} threshold being at 4. This is in line with the findings of Trapp (2002) for the dynamic case (i.e., k unequal to zero),

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[12] Note that a check of the units for Eq. (5-16) yields some inconsistencies if K_{rw} is not unitless, i.e., the units cancel out. However, as stated in the paper by Trapp (2002), it has units l per kg (according to equation 2b in that paper).

however, at a different threshold. One may, therefore, consider to introduce a two-threshold approach where for instance at a log K_{ow} in the range of 2 to 4 a correction factor of 0.1 could be used (note that in the range between log K_{ow} from 1 or 2 to 4 the distribution behaviour of substances between aqueous phase and lipid phase of plants is in transition, cf. Figure 2 in Riederer, 1995). Another difference is that the formula by United States - Environmental Protection Agency (1998) is valid for any edible belowground plant part (including potato tubers) whereas the advective uptake process is not allowed to occur in potatoes which are considered to be part of the stem (Paterson et al., 1994; Trapp, 2002).

It appears that the kinetic approach by Trapp (2002) can reasonably well be approximated by the introduction of a correction factor to an equilibrium model as done by United States - Environmental Protection Agency (1998). If equilibration between soil solution and roots is quick (only a few hours up to 24 hours according to Bromilow and Chamberlain (1995) and Briggs et al. (1982), respectively) the assumption of equilibrium seems to be valid. Thus, there is no need to distinguish a root compartment explicitly in the case of lipophilic compounds.

Metals or trace elements

Before continuing with the consideration of how existing models treat metals, a short overview on metal uptake via roots and possible translocations within plants shall be given.

It seems that anthropogenically added metals in the environment are more readily available to plants than are those released due to weathering of rocks and/or soils (Berrow and Burridge, 1991; Alloway and Steinnes, 1999; Greger, 1999). However, factors like the metal itself (e.g., Weigert, 1991), its total amount present in soil (Berrow and Burridge, 1991; Sauerbeck and Lübben, 1991) and its speciation (Berrow and Burridge, 1991; Kabata-Pendias and Pendias, 1992; Ritchie and Sposito, 1995; Markert, 1998; Helmke, 1999) have a marked influence. Furthermore, soil conditions (like cation exchange capacity, Peterson and Alloway, 1979 and Chaney et al., 1999, and organic matter content, Berrow and Burridge, 1991), environmental factors (like temperature, Chang et al. (1987) cited in Greger (1999)), drainage status (Berrow and Burridge, 1991) or the soil reaction (pH, Bingham et al., 1986; Berrow and Burridge, 1991; Reimann and de Caritat, 1998) also have significant influences on root uptake. Their influence, however, is also intervened by the metal and plant species (e.g., Sauerbeck and Lübben, 1991), plant age and plant speciation (Zimdahl and Koeppe, 1979). Plant speciation affects root uptake to such a degree that one can even distinguish between excluders and accumulators (Greger, 1999).

This brief overview has shown that modelling root uptake may become a rather complex issue. Owing to the rather simple overall modelling approach adopted (cf. section 2.3), only more general influences of plants with respect to root uptake will, therefore, be discussed in the following.

Some macronutrients are taken up actively by plant roots (e.g., Trapp and Matthies, 1998; Strasburger, 1991). Of the metals, this applies especially to potassium and due to its association also to rubidium (Strasburger, 1991). Less specific uptake is observed for other nutrients such as some heavy metals which are needed (at least in traces) by plants for example for enzyme creation. These include iron, manganese, zinc, copper, molybdenum, cobalt and nickel (Strasburger, 1991). Cadmium shows a geochemistry that is similar to zinc although being more mobile under acid conditions and reacting more readily with sulphur (Kabata-Pendias and Pendias, 1992), as well as having a stronger affinity to manganese oxides than to iron oxides in soils (Sauerbeck and Lübben, 1991). This similar behaviour is also postulated for translocation interactions of these two heavy metals (Welch and Norvell, 1999). In general, heavy metals are mostly taken up passively by plant roots although Greger (1999) reports non-passive uptake of cadmium (e.g., by soybean, Cataldo et al., 1983, or barley, Cutler and Rains, 1974), zinc and copper (e.g., by rice, Bowen, 1987) stating at the same time that the mechanism of metal uptake is not yet known. Upon entering the root core, heavy metals may be translocated by means of the transpiration stream according to the water potential gradient and, thus, accumulate mostly in plant leaves. The degree of translocation is amongst others dependent on the heavy metal. Greger (1999) estimates that between 75 % and 90 % of the heavy metals taken up through the roots stay in root tissue (cf. Mosbaek et al., 1989). A root/shoot ratio of 100 has been found for chromium in many crops (Zayed et al., 1998).

In order to explore whether heavy metals that have been transported from roots to shoots may return to the roots, their transport in the assimilate flux (i.e., in the phloem) shall be considered next. Generally, storage organs receive substances (nutrients and xenobiotics) via the phloem flow (Sauerbeck, 1989). Cations show different mobility in the phloem. Greger (1999) considers phloem transport of heavy metals as "probably difficult" (p. 15). In fact, there is a tendency that heavy metals are more immobile than light metals and if they tend to be more mobile they are at least to some degree essential to the plant: the light metals potassium, rubidium, caesium, sodium and magnesium are relatively mobile, the essential heavy metals iron, manganese, zinc, copper, molybdenum and cobalt are moderately mobile, whereas the inhomogeneous metal group of lithium, calcium, strontium, barium, lead, polonium and silver can be considered immobile (Table 2.1.26 in Strasburger, 1991). Calcium, barium and lead (and others) are immobile in the phloem due to the formation of insoluble phosphates. Other factors may also play a role such as the relatively high pH of 8 in phloem (Bromilow and Chamberlain, 1995) and competition between cadmium and zinc (Welch and Norvell, 1999) with a usual ratio of occurrence of 1:100 (Chaney et al., 1999) which might be different in plants due to different degrees of discriminative uptake. Welch and Norvell (1999) report phloem transport of Cd but do not state to what extent this transport occurs. The immobility of some metals in the phloem leads to an accumulation in the leaves which may be responsible for the need of any perennial plant (including 'evergreens') to clear their leaves from time to time (Strasburger, 1991).

Although the picture is not absolutely clear, one may conclude that phloem flow of (cationic) heavy metals can be neglected. There are no indications made in the reviewed literature to what extent anionic heavy metal forms might be transported in the phloem. For chromium and the trace element arsenic there are some indications with respect to the behaviour of their oxo-anions in plants. For chromium, a full reduction of hexavalent chromium to less mobile trivalent chromium is postulated to occur in plant roots (Zayed et al., 1998). This reduction to the less mobile form may be responsible for the high root/shoot ratio of about 100 reported for many crop species (Zayed et al., 1998) indicating little translocation whatsoever. As arsenic behaves like phosphorus (e.g Léonhard, 1991; Efroymson et al., 1997), it is expected to be as easily translocated also in the phloem as the latter. However, as arsenic competes with phosphorus which occurs at very much higher concentrations in arable soils and as it tends to form insoluble complexes, its root uptake is highly reduced (Léonhard, 1991). This is expressed by the little soil to aboveground transfer that is reported (e.g., by Speir et al. (1992) for experiments with the wood preservative Chromated Copper Arsenate), however, contradicting results exist. Another aspect with respect to arsenic is that most of its forms present in plants are organic which are not found to be toxic to humans (Chaney and Ryan, 1994; Harrison, 2001a).

From the models presented in Table 5-8, there are only two methods that consider metal uptake. Whereas Reinds et al. (1995) only considers the root uptake process by forest canopy, United States - Environmental Protection Agency (1998) provides estimates in any edible plant part of crops assuming equilibrium between soil and the respective plant component. Due to the paucity of available models, the approach taken by United States - Environmental Protection Agency (1998) is, thus, prioritised.

5.2.3 Removal due to harvest and/or litterfall

Apart from internal plant flows, the only advective losses of plant parts are due to harvest and litterfall. Harvest leads to a net removal of substances entrained in the harvested biomass from the soil which is why it is deemed necessary to include this process in the environmental fate model also.

There are only two models of those listed in Table 5-8 that consider removal by harvest: that described by Severinsen and Jager (1998) and TRIM.FaTE (United States - Environmental Protection Agency, 2002b). A non-changing plant biomass is assumed as is done in other publications either explicitly (Reinds et al., 1995; Bennett et al., 1998; Wania et al., 2000; Charles and Jolliet, 2003) or implicitly (Maddalena et al., 2002). Therefore, the rate constant for growth equals the sum of the rate constant for harvest and the rate constant for death (Severinsen and Jager, 1998). Whereas TRIM.FaTE (United States - Environmental Protection Agency, 2002b) assumes that all of the plant biomass of agricultural produce is removed and does, hence, not contribute to the soil loading due to litterfall, Severinsen and Jager (1998) only assume a portion of the aboveground biomass to be harvested (see below).

This approach might be defendable when dealing with annual (herbal) plants. However, for perennial plants like trees which cannot be assumed to stay in the exponential growth phase (cf. Trapp and Matthies, 1995), a certain amount of the built biomass will persist into the next growing season. In order to apply a steady-state approach, both models that include forests only consider leaves (Reinds et al., 1995; Wania et al., 2000), without taking account of the annual increase in stem diameter. Also Severinsen and Jager (1998) include trees of which parts are harvested. They additionally investigate the inclusion of tree trunks but conclude that this remains an area of investigation so that tree trunks are not considered in the following due to its poorly conceived status.

In the case of the plant model by Severinsen and Jager (1998), the harvest and death rate are linked to the growth rate by means of the harvest efficiency or its complementary value, respectively. Although not explicitly explaining what this parameter describes, it is figured that it is the volume share of the aboveground plant parts that is removed from the soil within one year, the remainder undergoing litter fall. The harvest efficiency is set to 59 % for agricultural aboveground produce and 34 % for aboveground forests. To what degree nutrient and/or contaminant rich matter like leaves and bark are left in the forests upon tree cutting may need to be investigated separately.

5.2.4 Metabolism or degradation

All but a few models in Table 5-8 include explicitly the process of degradation or metabolism. The reason for leaving this process out is presumably that they are concerned with metals (Reinds et al., 1995), focus on air-leave exchange processes (Tolls and McLachlan, 1994; McLachlan, 1996), or assess equilibrium plant concentrations (United States - Environmental Protection Agency, 1998) that may implicitly take account of degradation.

Thus, degradation or metabolism is a process that needs to be considered for degradable substances. Depending on whether speciation is taken into account, chemical transformation processes may also need to be considered when modelling heavy metals.

The issue of speciation also raises the issue of bound residues when modelling organic chemicals (cf. section 4.2.3). Trapp (1995) states that "the metabolism in plants will in many cases result in bound residues" (p. 146). Bound residues are residues non-extractable (by some solvents) that are covalently bound to organic matter (either of plant tissue or soil organic matter) making them less bioavailable and/or more stable. It is beyond the scope of the present study to elaborate and suggest an approach whether and how to include these in the overall formulation of degradation and/or the following exposure/impact assessment.

5.2.5 Translocation within plants

Assuming equilibrium within plants is problematic as plants do not have blood circulation (Sharpe and Mackay, 2000). Distinguishing between different plant parts might, therefore, be desirable (Trapp, 1995; Charles and Jolliet, 2003). If one distinguishes between roots, stem and leaves there are principally two interfaces across which exchange between these components may occur: root to stem or shoot in general and redistribution in aboveground plant parts.

Exchange between root and stem/shoot

Except for Paterson et al. (1994), the models presented in Table 5-8 do not assume exchange between roots and shoots. Most of them employ the transpiration stream concentration factor (TSCF) which relates the xylem concentration in the aboveground plant parts to the soil solution concentration, thereby skipping/jumping over/missing out the roots. One reason for disregarding the transfer from aboveground plant parts to roots is that the mass flow in the xylem is at least one order of magnitude higher than in the phloem (Trapp, 1995). Thus, a significant transport does not occur if their transport directions are opposite.

It seems debatable whether to include a transfer from roots to shoots for (heavy) metals. Greger (1999) found that during their transportation through the plant, metals get bound largely on the cell walls, which explains why most of the metal taken up is commonly found in the roots (about 90-75 %) and smaller amounts are distributed in the shoot. For further discussion on root-shoot exchange of heavy metals refer to section 5.2.2.

Exchange between aboveground plant parts

Due to the fact that there are only a few models in Table 5-8 that distinguish between stem and foliage (i.e., Paterson et al., 1994; Trapp, 1995; United States - Environmental Protection Agency, 2002b; unclear for Charles and Jolliet, 2003) and only one additionally considering fruits (Trapp, 1995), only a few descriptions are available for substance distribution in aboveground plant parts all of which, however, do not address the issue of redistribution of (heavy) metals within plants (refer to section 5.2.2 for more information about redistribution of metals). Although not explicitly distinguishing between stem and foliage but rather between protected and unprotected aboveground plant parts, the methodology by United States - Environmental Protection Agency (1998) has also been designed to include heavy metals and trace elements. It is, therefore, adopted for the assessment of these contaminants.

5.2.6 Conclusions on how to address plants in a multimedia environmental fate model and innovations

In order to conclude this sub-Chapter on modelling of terrestrial plants, first conclusions with respect to modelling of heavy metals and trace elements, i.e., the substance class prioritised in this study, will be drawn. In order to provide suggestions in terms of the assessment of 'ordinary' organic substances which may be considered in future model developments, also conclusions with respect to modelling of plants with respect to these substances are drawn.

Unlike many existing plant models (cf. Table 5-8), the harvest of agricultural produce is considered an important removal process from the environmental fate model at least for persistent substances. In section 9.3.3, it will be explored to what extent the exposure assessment in terms of the absolute exposure and its dynamics will be influenced by the inclusion of this harvest process. One has to note that if no removal by terrestrial plants was included in the environmental fate model this would mean that the total amount of a substance removed due to human food consumption is returned to the field. This could be achieved by soil amendments with sewage sludge. However, this return flow will not be complete especially because some sludges are not allowed to be spread onto the fields due to their loading with contaminants, be it the substance to be modelled or others also occurring in the sludge. Furthermore, the place where these substances return to the field will in many cases not be the same as the one where they were removed from due to the trade of food items (cf. section 7.2). This is particularly not the case if areas with an intensive agricultural production and high population density are not spatially distributed in a rather homogeneous way. This is rather often the case.

Modelling heavy metals and trace elements

In general, it appears that roots can be assumed to be in equilibrium with soil (equilibration time in the order of hours according to Briggs et al., 1982, Bromilow and Chamberlain, 1995 and Trapp, 2002). As a consequence, exchanges between shoot and root as included by Paterson et al. (1994) can be neglected. For thick roots, Trapp (2002) proposes a dynamic approach which presumably can be approximated by the inclusion of a correction factor as done by United States - Environmental Protection Agency (1998). Thus, soil and roots can be considered as one (as done, e.g., by Trapp and Matthies, 1995; Severinsen and Jager, 1998) for equilibrium is assumed to occur within compartments in level III/IV multimedia models. The only adjustment to be made is to consider harvest which is in line with Severinsen and Jager (1998) and deemed necessary to be included in the environmental fate model as it leads to a removal of substances out of the modelled system. This also applies to the aboveground plant parts that are harvested.

The treatment of aboveground plant parts is more complex. In particular the question how to treat deposits or residues on plant leaves is not yet scientifically settled although attempts have been made (e.g., United States - Environmental Protection Agency, 2002b; Charles and Jolliet, 2003). Exchange between foliage and other plant parts is basically due to phloem flow. If exchange between shoots and roots due to phloem flow can be neglected (for non-weak acid substances according to Bromilow and Chamberlain, 1995) the same may apply to foliage-stem transfers. The case seems to be different for foliage to fruit transfers mediated by phloem flow (Trapp, 1995), however, very little amounts reach the fruits.

For (heavy) metals and trace elements, there exists only one established methodology for the assessment of metals in agricultural produce in the non-exhaustive list of plant models given in Table 5-8 although attempts to model mercury have been found elsewhere as well (e.g., Maddalena et al., 2002). This was proposed by United States - Environmental Protection Agency (1998) and is recommended at least for this type of substances.

Reinds et al. (1995) provide a rather incomplete model for forests which is due to the fact that they propose a mass balance for the soil rather than for the plant biomass. Furthermore, Cousins and Mackay (2001) recommend to include plant compartments into environmental fate models only when the substances are considerably taken up either via foliage or via roots. Another criterion is to what degree a vegetation compartment influences exposure which is practically non-existing for non-agricultural vegetation. As hardly any translocation from leaves to other plant parts is assumed to occur for heavy metals (see section 5.2.2) and their distribution within plants shows considerably higher concentrations in roots (e.g., Mosbaek et al., 1989; Zayed et al., 1998; Greger, 1999) which are assumed to be in equilibrium with soil for reasons given above, it appears that there is no need to include a natural vegetation compartment into the environmental fate model for heavy metals. Accelerated atmospheric dry particle deposition due to forests ('filter factor') appears not be significant for smaller particles (< 5 μm) in which most of the metals of concern are concentrated (Jonas and Heinemann, 1985) although other authors consider the filter effect to be effective (Reinds et al., 1995; Schütze and Nagel, 1998). Thus, no attempt will be made to include natural vegetation compartments when dealing with non-volatile metals. Methyl mercury as well as elemental mercury are considered to behave like semi-volatile substances.

As a result, if plants are considered when assessing the environmental fate of trace elements this is done by means of combined uptake-removal processes without distinguishing separate compartments. Processes considered are:

- root uptake by and harvest of belowground produce,
- root uptake by and harvest of aboveground produce for non-volatile substances,
- removal from dry atmospheric deposition due to harvest of exposed aboveground produce, and
- removal from wet atmospheric deposition due to harvest of exposed aboveground produce.

Note that the former two constitute processes in the environmental fate matrix whereas the latter two influence the atmospheric deposition as an upper boundary condition. The respective formulations related to processes considered in the fate matrix are given in Table 5-9 and described in detail in section A.3.8 while the equations regarding the influence on the overall input to the water and soil environment are given in Table 4-3 (Eqs. (4-7) and (4-8)), with more details provided in section A.6.5.

Modelling non-dissociating organic substances

Based on the fact that equilibrium between soils and roots is accomplished within a few hours (Briggs et al., 1982; Bromilow and Chamberlain, 1995) and all but one of the models presented in Table 5-8 do not consider a transfer from shoots to roots, it appears that there is no need to include a separate root compartment also for organic compounds. It is, thus, proposed to follow the same approach for non-dissociating organic substances as for heavy metals and trace elements.

From what was presented in section 5.2.1, one may conclude that there is no need to distinguish a leaf surface compartment for semi-volatile organic compounds that are not applied to vegetation directly (such as pesticides). This is mainly due to the difficulties with characterizing this compartment (Riederer,

Table 5-9: Process formulations for terrestrial plants of agricultural use as used in the present assessment

Name	Refer to section ... for more details	Formulation[a]	
Root uptake by and harvest of belowground produce	A.3.8 (p. 404ff)	$k_{\text{i, uptake + harvest root crops}} = \frac{1}{fr\_V_{\text{solid phase/bulk}}(i) \cdot \rho_{\text{solid phase}}(i, z)} \cdot emp_{\text{BCF, root crops}}(p, r, e) \cdot BCF\_dw/dw_{\text{root/soil}}(p, r, e) \cdot fr\_w_{\text{solid phase/bulk}}(r, e) \cdot P(r, n)$	(5-18)
Root uptake by and harvest of aboveground produce for non-volatile substances	A.3.8 (p. 404ff)	$k_{\text{i, uptake + harvest aboveground crops}} = \frac{1}{fr\_V_{\text{solid phase/bulk}}(i) \cdot \rho_{\text{solid phase}}(i, z)} \cdot BCF\_dw/dw_{\text{plant/soil}}(p, r, e) \cdot fr\_w_{\text{solid phase/bulk}}(r, e) \cdot P(r, n)$	(5-19)

[a] *ATMDEP*: atmospheric deposition [kg/m²/s]; *BCF_dw/dw*: bioconcentration factor [-]; *emp*: empirical factor [-] or [s]; *fr_V*: fraction of a volume [-]; *fr_w*: mass fraction of a substance [-]; *k*: process rate as used in the coefficient matrix [m³/s]; *P*: annual production rate of a crop [kg FW/s]; *r*: process rate [1/s]; ρ: density [kg/m³]; *S*: source of substances into the water and soil fate model [kg/s]; *Y_fw*: yield of produce [kg FW/m²]; symbols in parentheses denote a parameter's dependency on the compartment ('*i*' replacing agricultural soil '*ag*' and pastures '*p*'), exposure assessment framework ('*e*'), administrative unit ('*n*'), pollutant ('*p*'), receptor (or crop, '*r*'), emission scenario ('*s*') and/or the zone ('*z*')

1995) and because wet and/or particle-bound deposition is only significant for low volatile, hydrophilic substances (Paterson et al., 1994; Trapp and Matthies, 1995). For pesticides, however, the inclusion of a 'leaf surface' compartment is only necessary if there is exchange between the surface residues on the one hand and plant interior or air on the other.

This leaves us with two compartments for most of the semi-volatile substances: the stem and the leaf compartment. There are two reasons why these may need to be distinguished:

- different parts of the plants are eaten and
- different parts of the plants exhibit different concentrations (cf. Trapp, 1995).

Although there is no 'all-in-one device suitable for every purpose'[13]-like plant meaning that usually not both the stem and the leaves of one plant are used as food, the need to distinguish between stem and leaves (as done by United States - Environmental Protection Agency, 1998) is evident and is, thus, suggested to be considered by default for all non-pesticide organic compounds.

Note that modelling degradation processes for organic substances in plants may require a re-consideration. As the equilibrium between soil and roots can be regarded as to include also degradation in the case of organic substances, it may be argued that considering an explicit degradation removal process additionally leads to double-counting of this process and should, therefore, be skipped.

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[13] Translation for German 'Eierlegende Wollmilchsau' or literal translation 'oviparous wool-milk sow' (http://dict.leo.org/ visited as of August 2004).