4 Multimedia environmental fate assessment framework: outline, atmospheric modelling and spatial differentiation

Based on the review of methods and models and the concluded needs for developments as described in the previous Chapters, the methodology that allows the assessment of exposures via soil and water which in turn lead to monetisible impacts will be described in the following. The methodology is implemented in a new module complementing the software tool EcoSense (European Commission, 1999a). This module is called 'integrated WATer and SOil environmental fate, exposure and impact assessment model of Noxious substances' (WATSON). For the easiness of referring to the new methodology, it will be referred to the implemented model name throughout this document noting that the modelling concept and its implementation into a tool are two distinct things. The way how the methodological approach taken has been implemented in order to become the WATSON tool is described in section 4.4.

The methodological approach suggested here builds on an existing air quality-related external cost assessment scheme (European Commission, 1999a). Its regional air quality model will be presented in section 4.1. WATSON is linked to this air quality model whose deposition fields serve as input to the terrestrial and aquatic environment (Fig. 4-1). Reasons under which conditions such a coupling is justified and how the coupling is performed are argued in sections 4.1.1 and 4.1.2, respectively. Based on the deposition field or on direct emission specifications to soil and/or water, the approach assesses the environmental fate in different soil and water compartments (Fig. 4-1). As was reasoned in section 2.3.2, the approach for the environmental fate model as introduced by Mackay (1979) is followed. The way how the assessment area, i.e., mostly Europe, is subdivided into zones is described in section 4.3. Their further subdivision into compartments is then subject of the subsequent Chapters. Within these, also special attention is spent on how to explicitly address metals.

In line with the suggestions given by an expert group of multimedia fate and exposure modellers (Cowan et al., 1995b), the detailed exposure assessment

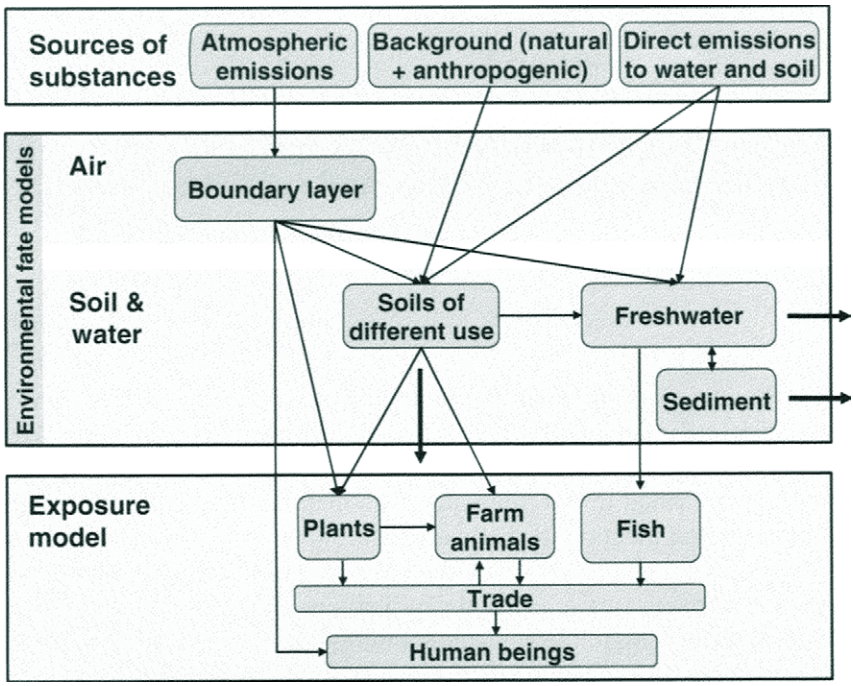

Fig. 4-1: Conceptual structure of the environmental fate and exposure assessment of the WATSON model and its linkage to the air quality model (arrows connecting boxes denote a substance's environmental pathway, arrows not connecting boxes indicate ultimate removal processes from the model's scope)

is performed separately from the environmental fate modelling although trade of food items might be considered an additional type of an environmental fate process involving rather long-range transports. The exposure together with the impact assessment are subject of Chapter 7. The approach taken for the monetisation of the effects is described in Chapter 8.

4.1 Dispersion in air and air to ground interface

In line with for example van Pul et al. (1998) and Bennett et al. (1998), atmospheric transport is modelled with the help of a Lagrangian trajectory model implemented in the EcoSense multi-source version (Windrose Trajectory Model, WTM, Trukenmüller and Friedrich, 1995). In contrast to fully integrated multimedia exposure models, the use of air dispersion models is advantageous when

Table 4-1: Treatment of different particle size classes by the Windrose Trajectory Model (WTM)

Size class [µm]	Median aerodynamic diameter [µm]	Mass distribution scheme A [%]	Mass distribution scheme B [%]	Washout ratio [-]	Dry deposition velocity [m per s]
< 0.95	0.2	70	42	$5.05 \cdot 10^4$	0.00065
0.95-4	1.5	20	33	$3.78 \cdot 10^5$	0.0025
4-10	6	5	14	$3.78 \cdot 10^5$	0.0071
10-20	14	3	6	$3.78 \cdot 10^5$	0.0132
> 20	40	2	5	$3.78 \cdot 10^5$	0.067

rather complete emission information in terms of space are available (Hertwich et al., 2000). The WTM is based on work done by Derwent and co-workers (Derwent and Nodop, 1986; Derwent et al., 1988) and operates on the EMEP 50 x 50 km^2 grid (see Fig. B-1). The model is a receptor-oriented Lagrangian trajectory model employing an air parcel with a constant mixing height of 800 m moving at a representative wind speed. In contrast to forward trajectory models, the receptor-oriented backward trajectory model type is able to take reaction kinetics higher than first order into account enabling to model pollutants that are reaction products ('secondary pollutants') of reaction partners stemming from different sources (Trukenmüller, 1998). The results are obtained at each receptor point by considering the arrival of 24 trajectories weighted by the frequency of the wind in each 15° sector. The trajectory paths are assumed to be along straight lines and are started at 96 hours from the receptor end point. The meteorological data for instance for the windroses and wind speeds are annual averages which are best taken from long-term observations which makes the data representative (climatological data, Trukenmüller, 1998).

In order to allow for particulate transport which is important for rather involatile trace elements being released to air, WTM distinguishes five particle size classes (as done in van Jaarsveld, 1990) that are treated separately in terms of wet and dry deposition velocities (Table 4-1). Also, different substances follow different mass distributions. Organic substances, lead and mercury associated with particles follow scheme A whereas the other metals are assumed to follow scheme B. It needs to be noted that the suggestion with respect to the size class

distributions stems from the late eighties/early nineties when most of the lead emissions in Europe occurred from the burning of leaded gasoline. Nowadays, it is, therefore, more likely that lead follows scheme B (Lee, 2003; Samara and Voutsa, 2005) which is also in line with the chemical forms mostly released from high-temperature processes (Pacyna, 1987). For arsenic and cadmium, scheme B's mass distribution is in agreement with recent findings whereas that of nickel shows a four-modal shape (European Commission, 2000b and literature cited therein).

4.1.1 Linking of an air quality model and a soil/water model

One drawback for coupling an air quality model to a multimedia (soil and water) model could be that it is not fully integrated. This means that the assumed/expected multiple intermedia exchanges of for instance the so-called multimedia organic pollutants between air on the one hand and soil and water on the other may not be allowed for. For the bulk of substances which are not true 'multi-hop pollutants' (Klepper and den Hollander, 1999), however, the intermedia exchange (or feedback) is assessed to be small (Margni, 2003; Margni et al., 2004). Heavy metals can principally re-enter the atmosphere via volatilisation and resuspension when attached to particles that were previously deposited. Apart from mercury, however, heavy metals do not have a significant vapour pressure so that volatilisation can be neglected. Suzuki et al. (2000) investigated the influence of wind erosion on the fate of rather persistent organic chemicals, i.e. PCDD/Fs, with the help of a (fully integrated) multimedia model. In a sensitivity analysis, they found that this process is negligible. It is noted that these chemicals possess remarkable vapour pressures if compared to many trace elements and especially those that are assessed in this work (cf. section 3.2.4). This could mean that the found insensitivity of dioxins to the soil wind erosion process is due to volatilisation going on to some extent. Nevertheless, this process is not considered in the methodological framework presented due to the fact that soil wind erosion mainly occurs on plain areas in arid to semi-arid climates with little to no vegetation cover (Scheffer and Schachtschabel, 1989). Within Europe, these climates can mostly be found around the Mediterranean Sea. However, the share of non-vegetated land is grossly small (cf. right of Fig. 5-2) noting that also arable land may show only a small vegetation cover under black fallow conditions or prior to total plant coverage.

Based on the findings of Margni and co-workers (Margni, 2003; Margni et al., 2004), the feedback of volatile substances can be taken into account in the present modelling framework when defining the air quality model's exchange rates with the respective ground surface for the particular 'multi-feedback' substance (see Table 4-2 for examples of feedback fractions).

Table 4-2: Feedback fractions of selected substances (Margni, 2002)

Substance	Feedback fraction [%]
Benzene to air	2
Benzene to water	1
2,3,7,8-TCDD	0.2
Benzo(a)pyrene	$9.1 \cdot 10^{-4}$ [a]

a. Value is supported by findings of Pekar et al. (1999) in that no re-emission from soil or sea water to air occurs for 11 years.

It is, therefore, concluded that the coupling of a single-medium air quality model to a water and soil multimedia type of model is a justifiable approach for assessing average environmental concentrations of non-'multi-feedback' pollutants at the regional scale.

In the next section, it is described how the linkage is performed together with the underlying assumptions.

4.1.2 Interface between air and soil/water

The results with respect to atmospheric depositions from the air quality model form the basis for the indirect input to the terrestrial and aquatic environment.[6] As the air concentrations and depositions are given on the EMEP 50 x 50 km^2 grid, this information needs to be transformed to match the regions distinguished (see Fig. 4-2 or 4-3). This is done on an area-based weighting scheme without distinguishing between different land uses. With the exception of orographic fog or cloud droplet impaction (e.g., Lovett et al., 1982), the assumption of a homogeneous deposition pattern holds for wet deposition. However, this assumption appears to underestimate or overestimate to some degree dry deposition rates at forest and non-forest sites, respectively, as expressed by filter factors which are assumed to lie in the range of 1.6 for deciduous forests to 2.1 for coniferous forests for metals (Reinds et al., 1995) especially with respect to gaseous deposition (e.g., Horstmann and McLachlan, 1998). However, it was found that forests can no longer be regarded to have a filter effect relevant to aerosols with an aerodynamic diameter of less than 5 µm (Jonas and Heinemann, 1985) with the excep-

6 From a technical point of view, these are stored in a database as described in section 4.4.

tion of forest edges near emission sources (e.g., Hasselrot and Grennfelt, 1987) whose area share is small compared to the full forested area. Most of the metals being released in a particle-bound way fall into this particle size class (see Table 4-1). As a consequence, the values assumed by Reinds et al. (1995) are considered too large as they were also based on work done by Ivens et al. (1989) for basic cations that belong to larger particle size classes. As also the dry gaseous deposition of non-volatile substances like most trace elements can be neglected, the conversion of the deposition rates from grid cells to (undifferentiated) regions on an area-weighted basis is considered a valid approach.

4.2 General description of the soil and water environmental fate model

The fate model for the terrestrial and aquatic environment is formulated like a spatially-resolved Mackay-type multimedia model based on homogeneous compartments at equilibrium and first order kinetics for the exchange between compartments and respective loss processes. In line with Brandes et al. (1996), the mass balance is based on concentrations. In matrix notation, the respective inhomogeneous system of ordinary linear first order differential equations reads:

$$\vec{v} \cdot \frac{d\vec{c}}{dt} = A \times \vec{c} + \vec{b} \qquad (4\text{-}1)$$

where

A : coefficient matrix of dimension n x n [m^3/s] (process rates are defined as described in Tables 5-5, 5-9 and 6-3 and in more detail in the sub-sections to A.3)

$\vec{b}$: perturbation vector of dimension n with exogenous inputs considering atmospheric deposition or direct emissions to the compartments [kg/s] (input rates are defined in Table 4-3 and described in more detail in the sub-sections to A.6)

$\vec{c}$: concentration vector of dimension n [kg/m^3]

t : time [s]

$\vec{v}$: volume vector of dimension n [m^3] (volumes are defined as described in more detail in the sub-sections to A.4).

In this equation, the volume vector and the coefficient matrix contain information on various process rates which depend on nature and substance-specific

properties. The perturbation vector defines the emission scenario analysed. As described in section 4.4 and demonstrated in section 9.3.3, the coefficient matrix can be defined in a very flexible way which allows the inclusion or exclusion of compartments as well as of processes. Also, the spatial differentiation into zones may be varied.

This system of linear differential equations can be solved for the steady-state situation or dynamically, referred to as level III or IV, respectively (e.g., Mackay, 1979, 1991; Trapp and Matthies, 1998). 'Steady-state' means that there is no concentration change in time (any more) given a constant and continuous emission into the modelled system. Eq. (4-1) hence becomes:

$$\vec{v} \cdot \frac{d\vec{c}}{dt} = 0 = A \times \vec{c} + \vec{b} \Rightarrow \vec{c} = A^{-1} \times -\vec{b}. \qquad (4\text{-}2)$$

The steady-state solution may serve to analyse which impacts present emission levels if enduring might have on future generations in a sustainability context for instance (European Commission, 2003d) or for time-integrated exposure assessments of pulse emissions (Heijungs, 1995).

The way the dynamic solution is computed is described in section A.1.2.

4.2.1 Defining the inputs to the terrestrial and aquatic environment

In section 4.1.2, the linkage between the air quality model and the water and soil environment has been described. Beside atmospheric inputs, also direct releases to the soil and water compartments can be taken into account. The way how these inputs are modelled by the presented methodology is shown in Table 4-3 and described in more detail in sub-sections to A.6. It is distinguished into regular processes and those modifying particularly atmospheric depositions. Note that the question whether and under which conditions the removals from the atmospheric deposition might lead to erroneous negative inputs is discussed in section A.6.5 (note the negative signs for these processes in Table 4-3).

4.2.2 General remarks on processes considered in the environmental fate modelling

Processes to be considered in an environmental fate model may be distinguished into three groups:

1. removal processes,
2. transport within zones, and
3. transport between zones.

Table 4-3: Process formulations determining the (exogenous) inputs into the water and soil compartments

Name	Refer to section ... for more details	Formulation[a]	
Regular inputs			
Direct emissions into soil or water	A.6.1 (p. 421)	$S_j(s, p, i, z) = S(s, p, i, z)$	(4-3)
Wet or dry atmospheric deposition	A.6.2 (p. 421) A.6.3 (p. 422)	$S_{a\text{-}i}(z, s, p, i) = A(z) \cdot fr\_\mathrm{A}(i, z) \cdot ATMDEP_{\mathrm{wet\|dry}}(s, p, z)$	(4-4)
Modifications of the regular inputs			
Wet atmospheric deposition to permeable soils considering preferential flow	A.6.4 (p. 423)	$S_{a\text{-}i}(z, s, p, i) = A(z) \cdot fr\_\mathrm{A}(i, z) \cdot ATMDEP_{\mathrm{wet}}(s, p, z) \cdot (1 - fr\_v_{\mathrm{pref\ flow/rain}}(z))$	(4-5)
Wet atmospheric deposition to the subsurface through preferential flow	A.6.4 (p. 424)	$S_{a\text{-}f}(z, s, p) = A(z) \cdot (1 - fr\_A(w, z) - fr\_A(gl, z) - fr\_A(u, z)) \cdot fr\_v_{\mathrm{pref\ flow/rain}}(z) \cdot ATMDEP_{\mathrm{wet}}(s, p, z)$	(4-6)

Table 4-3: Process formulations determining the (exogenous) inputs into the water and soil compartments

Name	Refer to section ... for more details	Formulation[a]	
Removal from dry atmospheric deposition due to harvest of exposed above-ground produce	A.6.5 (p. 427)	$S_{\text{a-ag}}(s,p,z,r,n,e) =$	$-ATMDEP_{\text{dry}}(s,p,z) \cdot \frac{1-10^{(r_{\text{plant surface loss}}(r,e)\cdot t_{\text{exposure duration}}(r,e))}}{r_{\text{plant surface loss}}(r,e)} \cdot fr\_w_{\text{intercept/deposition}}(r,e) \cdot \frac{P(r,n)}{Y\_fw(r,n,e)}$ (4-7)
Removal from wet atmospheric deposition due to harvest of exposed above-ground produce	A.6.5 (p. 429)	$S_{\text{a-ag}}(s,p,z,r,n,e) =$	$-ATMDEP_{\text{wet}}(s,p,z) \cdot fr\_w_{\text{adhere/wet deposition}}(p,r,e) \cdot \frac{1-10^{(r_{\text{plant surface loss}}(r,e)\cdot t_{\text{exposure duration}}(r,e))}}{r_{\text{plant surface loss}}(r,e)} \cdot fr\_w_{\text{intercept/deposition}}(r,e) \cdot \frac{P(r,n)}{Y\_fw(r,n,e)}$ (4-8)

a. A: area of the zone [m^2]; $ATMDEP$: atmospheric deposition [kg/m^2/s]; fr_A: area fraction of a compartment within a zone [-]; fr_v: fraction of a process velocity [-]; fr_w: mass fraction of a substance [-]; P: annual production rate of a crop [kg FW/s]; r: process rate [1/s]; ρ: density [kg/m^3]; S: source of substances into the water and soil fate model [kg/s]; t: duration [s]; Y_fw: yield of produce [kg FW/m^2]; symbols in parentheses denote a parameter's dependency on the compartment (generic: 'i' and specific: 'a': air; 'ag': arable (or agricultural) land; gl: glacier; n: (semi-) natural ecosystems; u: impervious surface (urban/built-up area)), exposure assessment framework ('e'), administrative unit ('n'), pollutant ('p'), receptor (or crop, 'r'), emission scenario ('s') and/or the zone ('z')

There are principally two ways how substances can be removed from the mass balance: by 'degradation' and by transport beyond the model's boundaries. The latter is related to transport within or between zones.

A better notion for 'degradation' which might imply that a substance has been fully mineralised and does not pose any harm any longer could be 'chemical transformation' or 'inactivation'. In particular the latter notion might well be suited to comprise all processes that keep toxic substances from becoming effective (again). Some reflections on inactivation processes especially with respect to trace elements will be given in section 4.2.3.

In an environmental fate model consisting of water and soil compartments, transport within and between zones is mostly driven by water flows although diffusion of substances between adjacent compartments such as freshwater and sediment also occurs. The zones have been defined according to basin boundaries (cf. section 4.3). These zones are interlinked by a cascade flow from upstream areas to downstream areas making use of the Pfafstetter code (Verdin, 1997). Since each zone constitutes a separate drainage area which may principally receive water from at most two upstream zones and may deliver to one downstream zone (cf. top of Fig. 4-4), all water flows are funnelled to the outlet of the zone. It is assumed here that the outlet of a zone is the only place where exchanges between zones occur. If ground water was considered, the assumption that there is no exchange of water between ground water bodies of adjacent zones would be in line with Arnold et al. (1993) and Blöschl (1996). This means that zonal boundaries act as barriers also for subsurface flows so that exfiltration into surface freshwater bodies would only occur within one zone. The situation would of course be different if an air compartment was added in an integrated way.

Also processes that take place in terrestrial compartments do not cross zonal boundaries. For instance, processes such as erosion and overland flow only deliver to the corresponding freshwater body of the same zone. Principally these flows may also connect different terrestrial compartments of the same zone. However, information on the situation of for example arable land towards natural ecosystems gets lost according to the 'semi-distributed' approach as suggested by Becker (1995) and followed in this work (cf. section 5.1). Transport within zones, thus, primarily connects the terrestrial compartments to the aquatic environment, i.e., mostly from soils to streams and rivers but also from soils to the subsurface which may or may not be beyond the model's boundaries.

The processes will be described in the respective sections on the different compartments below. Their formulation has been guided by the SimpleBox model (Brandes et al., 1996). Before these are described some reflections on inactivation processes with respect to non-degradable substances will be given as announced above.

4.2.3 Remarks on the consideration of inactivation processes

As metals or non-radioactive elements are perfectly persistent compounds that do not degrade, their possible transformation reactions shall be looked at more closely. The following transformation reactions are principally to be considered in the terrestrial environment:

- speciation, i.e., different chemical compounds of the same element which may also be distinguished functionally (e.g. according to bioavailability) or operationally (e.g. according to separation techniques; cf. e.g. Ure and Davidson, 1995),
- inactivation due to irreversible binding (e.g., Selim and Amacher, 2001), and/or
- precipitation of insoluble minerals (e.g., Robarge, 1999).

Considering speciation is in principle possible by adding the same amount of equations per considered species in the environmental fate model as for a single species version, provided the respective information on transformation reactions are available. This may in turn lead to very large equation systems posing higher requirements on the available computer and storage resources.

Irreversible binding, however, is another issue.'Irreversible binding' means that the release of substances that are sorbed to 'geo-media' is kinetically hindered and practically impossible (Lumsdon and Evans, 1995). When discussing the fate-modelling of metals in multimedia models for use in assessments of life cycles and external costs, it should be kept in mind that the time frame may be in the order of several hundreds or even thousands of years (van den Bergh et al., 2000; Huijbregts et al., 2001) given the potentially very long residence times of these contaminants, for example, in soils (Alloway et al., 1996). Any notion about irreversible binding or precipitation becomes less important in such a very large time frame.[7] Any short term experiments that indicate that part of the substance is 'irreversibly' bound are irrelevant since on the time scales that are involved minerals can completely dissolve, be transformed etc. and all elements are in principle available. That does not mean that at any time the metals are completely available. The processes described like complexation and precipitation are at any moment in time still at work.

The suggestion is not to include the processes of 'irreversible binding' and 'insoluble' mineral formation explicitly but to use solid-water partitioning coefficients that have been measured in natural soils (not influenced by recent anthro-

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[7] Although noting that such long time horizons potentially bring about the necessity to include geological processes.

pogenic additions of the relevant element) on the basis of total element soil concentrations (e.g., by hydrofluoric acid destruction).

There are also other reasons not to include irreversible binding into the environmental fate model even when assessing short time scales. Irreversible binding as any binding is dependent on available surfaces which is why this process is capacity-limited. The net 'irreversible' nature is due to sorption at specific sites that have a higher affinity for the respective metal (higher binding strengths). In particular these binding sites become less and less available with a higher degree of 'irreversible' binding occurring until the capacity is exhausted (Selim and Amacher, 2001). Models that are used to describe sorption processes (e.g., Langmuir and Freundlich isotherms as well as surface complexation models, Jenne, 1998a) take this binding capacity into account and are as a consequence non-linear. The degree of occupancy of the specific sorption sites is also the reason why solid-water partitioning values for some metals (like copper, cadmium and lead) are dependent on the overall metal concentration (Anonymous, 1999b; Selim and Amacher, 2001). This is also true for the dynamic equilibrium between a precipitate and the dissolved metal fraction. Introducing parameters that depend on a substance's concentration into an environmental fate model would require to formulate it with non-linearities. Thus, the approach followed in the development of the WATSON environmental fate model that is formulated as a set of ordinary first order linear differential equations would have to be abandoned. Another aspect of considering the inactivation processes explicitly is that plant uptake as used in many exposure models (e.g., United States - Environmental Protection Agency, 1998; International Atomic Energy Agency, 2001) is based on a transfer factor relating the total dry soil concentration to the plant concentration. In the analysis of the total dry soil concentrations, often strong agents like nitrohydrochloric acid ('aqua regia') or hydrofluoric acid are used which would even release at least to some degree the 'irreversibly' bound and precipitated fractions of the metals irrespective of their availability under natural conditions. Thus, there is a need to also include the inactivated metals in the bulk concentration numbers. However, if the process of inactivation of metals be it due to irreversible binding or due to precipitation was to be introduced into the steady-state environmental fate model it would need to be formulated as an overall loss from the system removing the amount of metals at the same time from the bulk soil. This, in turn, would not allow to consider this fraction in the bulk soil concentration for plant root uptake estimates. Another option would be to introduce another compartment which solely contains the highly unreactive portion of metals that is only released at an extremely low pace. This would, however, enlarge the numbers of compartments and, thus, equations to be solved. Furthermore, influences of an environmental medium's oxidative power (or redox conditions) that varies diurnally or

seasonally (e.g., Bartlett, 1999; Olivie-Lauquet et al., 2001) on speciation and/or inactivation cannot be dealt with if employing a climatological model that makes use of long-term annual meteorological and hydrological information. As a result, one would have to abandon the level III (steady-state) modelling approach which would require the development of a new model in order to allow for irreversible binding and redox conditions adequately.

Irreversible binding does not only apply to metals but also to the realm of organic chemistry forming the so-called 'bound residues' (e.g., Chung and Alexander, 1998; Eschenbach et al., 1998; Karimi-Lotfabad et al., 1998). In a critical review, Luthy et al. (1997) state that the fundamental knowledge about the nature of the sequestration of hydrophobic organic chemicals by geosorbents is still lacking. In a general model, the authors distinguish between partitioning that is assumed to be linear and non-linear adsorption (see above). Sorption and desorption show reaction rates that range from minutes to even years. Although these rates are derived from macroscopic observations that lack microscopic explanations especially when considering the heterogeneous mixture of potential organic sorbents present in soils, sorption processes involving kinetic considerations are usually not included in the more advanced level III/IV multimedia models as chemical equilibria are assumed within compartments (Mackay, 1991). It might, therefore, be worth considering whether to include 'irreversible binding' of organic chemicals as a kind of degradation process rendering the respective amounts unavailable to further dispersion and potentially toxic effects. As 'degradation' is considered for organic chemicals, one may need to explore whether the formation of bound residues is already implicitly contained in the degradation indicators (e.g., half lives).

4.3 Spatial differentiation of the terrestrial and freshwater environment

The fate model for the terrestrial and aquatic environment is formulated in a spatially-resolved way. 'Spatially-resolved' means that different zones are distinguished in order to allow for a site-dependent impact assessment. The way how these zones are delimitated will be described in the following. Subsequent sections will then deal with the subdivision of the zones into compartments. It shall be noted that similar to the SoilFug model (Di Guardo et al., 1994; Barra et al., 2000), WATSON only includes terrestrial and aquatic compartments.

When dividing an area in sub-entities, one needs to select criteria how this division is performed. Different approaches and/or recommendations for spatial differentiation in multimedia modelling efforts exist (see also Wania, 1996 and a general discussion in section 2.3.1):

- Pelichet (2003) recommends to use a grid-based differentiation of the air compartment and a watershed-based differentiation for the terrestrial environment. Based on this evaluation, the earlier version of IMPACT 2002 has been modified to separate the medium air according to a 2° by 2.5° grid (cf. Pennington et al., 2005).
- GLOBOX is based on countries with only one air and water compartment which are (uni- or bidirectionally) connected to all adjacent countries irrespective of watershed borders for water flows (Wegener Sleeswijk, 2005).
- BETR (north American multi-zonal multimedia model) mostly spatially differentiates its geographical scope based on watersheds (MacLeod et al., 2001; Woodfine et al., 2001). This applies to all compartments.
- EVn BETR (European-scale multimedia model) subdivides Europe into 5° by 5° grid cells (Prevedouros et al., 2004). Connectivities for air and water exist between adjacent grid cells.
- ChemCan (Woodfine et al., 2002) divides Canada into 24 ecological regions.
- There exist other environmental fate models of different spatial resolutions (Wania and Mackay, 1995; Wania, 1996; Scheringer et al., 2000b). However, these are 'investigative' fate models that try to predict what distribution patterns different substances follow and not exposure models that are needed to arrive at impacts.
- A more general recommendation was given at the SETAC workshop on multimedia models (Cowan et al., 1995b) in that the zones investigated should cover areas with more than a few hundred square kilometres due to the assumption of uniform mixing. However, this recommendation was given for spatially unresolved models. Spatially-resolved models, in contrast, aim at distinguishing areas with different concentrations. Thus, the recommendation given is considered not applicable here.

It may be concluded that there exist several approaches for spatial differentiation in the realm of spatially-resolved multimedia modelling ranging from administrative units (i.e., nations) over regular grids to natural properties especially water divides.

Apart from air advection, water generally constitutes the main carrier for substances across the landscape. The importance of water flows further increases for substances whose environmental fate is not largely determined by the rates of transformation. In any case, lateral surface and subsurface flows need to be considered which belong to the so-called 'lateral flows domain' (Becker, 1995). Modelling of lateral flows "must principally take into account the boundaries of hydrological systems like river basins, ground water systems etc., i.e. the drainage basin water divides" (ibid., p. 138). This is in line with Hunsaker et al. (1990) who note that zones for which impacts are assessed should be functionally defined, i.e.,

the "boundaries should be determined by physical or biological processes that affect the impact of the hazard such as the boundaries of watersheds, airsheds, and physiographic provinces" (p. 327). This will additionally support the transferability of the approach to other regions.

Consequently, watershed or drainage basin information are used for the delimitation of the terrestrial environment. Single watersheds vary substantially in size (e.g., the Danube compared to rivers that only stretch a few kilometres inland). Treating watersheds of considerably different size in the same way, i.e., as just one zone, has bearings on the environmental fate modelling. Due to the homogeneous mixing assumption, however, an artificial effect may result which may be called the 'instant long-range mixing effect'. Consider emissions taking place near the river mouth which are instantly mixed into the entire water contained in the watershed according to the homogeneity assumption within compartments. Whereas for smaller catchments the error introduced would not be too severe, this would lead to a situation in which emissions for example occurring in the Netherlands end up in Lac de Neuchatel in Switzerland if the Rhine - as a larger river - was not further subdivided into sub-catchments. Also, when assessing rather readily degradable substances these would occur at locations where they would never arrive due to the fast chemical transformation taking place.

Consequently, there is a need for larger watersheds to be further subdivided. Beside the subdivision itself, information on how the different zones are connected to each other is needed. The subdivision adopted in WATSON follows watershed information based on the HYDRO1k Basins dataset (EROS Data Center, 1996) which provides both of these sets of information.

Connectivities are defined according to the Pfafstetter code (cf. Verdin, 1997). This code allows to identify whether and where a zone is situated within a drainage basin. According to this code, each drainage basin of larger rivers is subdivided into nine sub-basins if at least four larger tributaries can be identified. These are coded with even numbers from downstream to upstream. The drainage areas between these basins (called interbasins) assume the respective odd numbers and constitute the main stem of the subdivided river. This procedure can be repeated for each basin and interbasin if again at least four tributaries can be identified. The Pfafstetter code can also be applied starting at the continental level. For Europe, the Rhine catchment, for instance is identified at the third subdivision level by the code "914" (Fig. 4-4). A further subdivision is also possible at least at the fourth level (as indicated in Fig. 4-4) and for some (inter-) basins even below. Therefore, also the connectivities by water currents between zones are given by EROS Data Center (1996).

The zones were visually checked to Cleveland et al. (1984) and European Environment Agency Data Service (1998) and corrected where deemed necessary (cf. Table B-1).

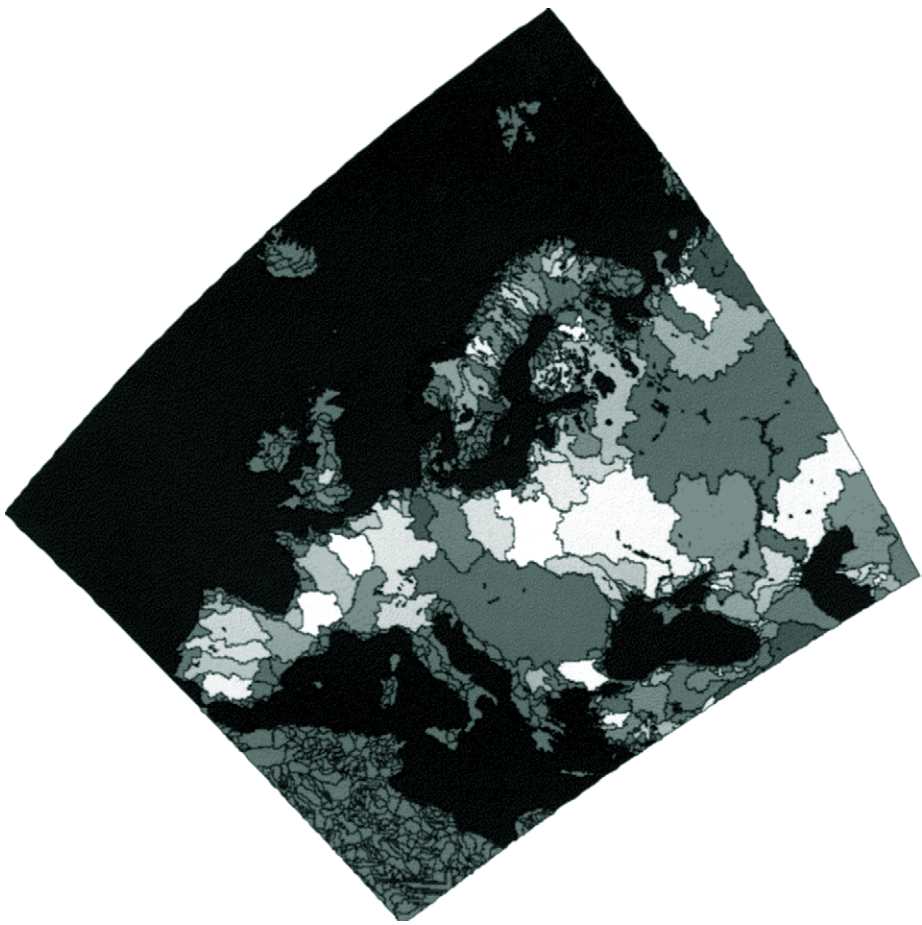

Fig. 4-2: Spatial resolution of the WATSON model based on watersheds; data taken from EROS Data Center (1996) and adjusted (see text)

A further subdivision into zones has been performed according to land cover information on freshwater bodies. In order to distinguish at least larger lakes with a potentially high water volume from rivers, lakes of an area larger than 100 km^2 were defined as described in section B.2.1. In case these are not just contained within one zone but spread over several zones, all these lake zones are allowed to also constitute separate zones.

The two presently available subdivisions of the spatial scope of the WATSON model into zones are shown in Fig. 4-2 and 4-3 (low and high resolution, respectively).

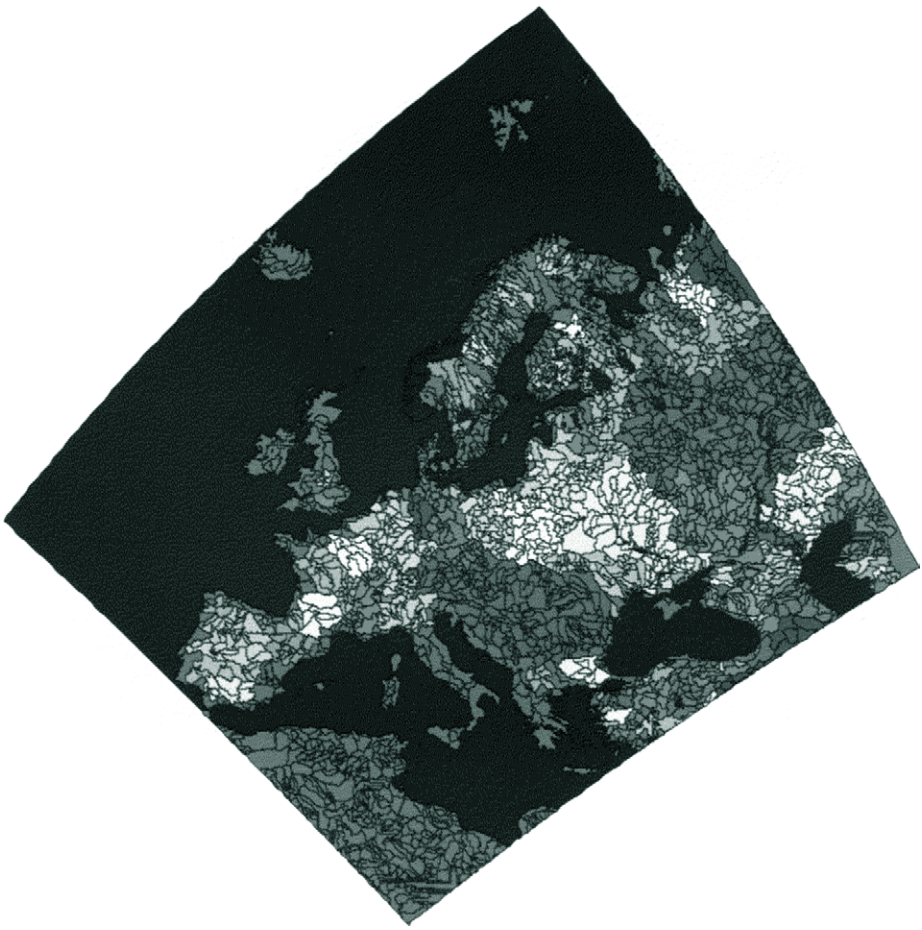

Fig. 4-3: Spatial resolution of the WATSON model based on watersheds which are further subdivided in the case of larger catchments; data taken from EROS Data Center (1996) and adjusted (see text)

4.4 Implementation

This section on the implementation of the conceptual model into a software tool shall neither serve as a manual to the usage of WATSON nor shall it provide details on the algorithms implemented. Instead, some technicalities shall be described.

In contrast to the majority of multimedia fate and exposure models which are implemented as spreadsheet models, for instance EUSES (Vermeire et al.,

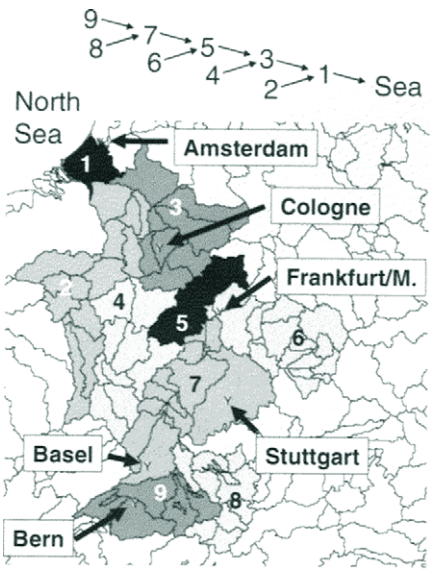

Fig. 4-4: Organisation of the Rhine catchment including the Meuse river according to the Pfafstetter code (note the Rhine catchment is identified by "914" at the continental scale, the shown digits constitute the fourth level subdivision, i.e., "914x"; the general Pfafstetter coding principle is also shown at the top)

1997), USES-LCA (Huijbregts, 1999), CalTOX (McKone, 1993b) and IMPACT 2000 (Pennington et al., 2005), the software tool developed here does not employ spreadsheets for the environmental fate and exposure assessment steps of the Impact Pathway Approach. While the existing EcoSense multi-source model is coded in C (MS Visual Studio 1.5) and the data storage is done with the help of a Paradox database, WATSON is coded in C++ (MS Visual Studio 6.0) and uses a LINUX-based Oracle database version 8.1.6i. This allows a flexible definition of process formulations and combinations as well as the use of different environmental settings (see explanation of *process sets* below). This way, data are kept separately from the simulation code (Robinson, 1999) which facilitates their changeability (Veerkamp and Wolff, 1996), however, on the expense of computation time.

Unlike many existing multimedia models, WATSON's mass balance is based on concentrations (like SimpleBox, Brandes et al., 1996) rather than on fugacities (e.g., Mackay, 1979) avoiding the aquivalence approach (Mackay and Diamond, 1989; Diamond et al., 1992). The solution of the system of linear differential equations is facilitated with the help of the NAg C library mark 6 (cf. section A.1).

Data processing of spatially distributed parameters has been done with ESRI ArcInfo version 7.1.1 and displayed with ESRI ArcView GIS version 3.1.1 employing various datasets. The datasets together with the derivation of the spatially variable parameters used in the environmental fate model are described in detail in Appendices B and C.

4.4.1 Definition of scenarios

WATSON allows the analysis of different scenarios. A *scenario* consists of the combination of several definitions:

- of emissions into different media (defined by a so-called *exogenous input type*; cf. section A.6) which may either be continuous and constant or consist of a constant pulse emission over a specified time period; WATSON allows for different allocation schemes for direct emissions to water and soil (e.g., according to population density or land uses); as with the exposure assessment, the specification especially of direct releases into water and soil follows administrative units (cf. Fig. B-4),
- of allowed environmental fate processes including the definition of the spatial differentiation in terms of compartments distinguished and degree of sub-division of the geographical scope into zones (defined by a so-called *process set*; cf. section 4.3 on spatial differentiation),
- of considered initial background concentrations, and
- of the exposure assessment to be followed (defined by a so-called *exposure frame* or expo frame).

The environmental fate matrix is, thus, defined by the process set in a very flexible way. Similar to TRIM.FaTE (United States - Environmental Protection Agency, 1999a), within WATSON the user can switch particular processes on and off rather than setting unrealistic values for example for vapour pressures of non-volatile compounds like most trace elements (as done, e.g., in Guinée et al., 1996; European Commission, 2003b). If the process set is defined in such a way that there is a compartment without any removal process the respective compartment is not further considered in the assessment.[8] The ability to change the compartmental mass balance in terms of processes combined as well as in terms of process formulations is a prerequisite in order to cover several substance classes (e.g., Trapp and Schwartz, 2000). The process set is computed and stored only once per substance and may be used by different scenarios.

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[8] This is actually an option which can be switched on and off by the user.

Parameters, processes, process sets, receptors, exposure frames, exogenous input types and auxiliary formulae which may help to internally derive parameter values are defined based on different assumptions. These assumptions especially when they might cause conflicts are also assigned to these components so that a check can be performed as to whether a combination of these components may lead to errors (e.g., considering preferential flow in the fate (cf. section A.3.7) but not in the exogenous input part (cf. section A.6.4)).

4.4.2 Temporal modes of operation

In order to address a variety of questions, different temporal modes of operation are possible with the WATSON model:

- steady-state is a situation in which no change in concentration occurs over time. That means that all outputs of a compartment equal the inputs. This situation may, thus, be relevant for sustainability-related questions (e.g., European Commission, 2003d). Furthermore, Heijungs (1995) has shown that the steady-state situation can also be used for time-integrated exposure assessments of pulse emissions. For life cycle analysis purposes where pulse emissions are dealt with, the perception prevails that temporal discounting should not be performed that may lead to neglecting even the larger share of potential future impacts of long-lived pollutants (e.g., Udo de Haes et al., 1999), especially of metals and radionuclides. Thus, steady-state solutions are regularly computed.
- quasi-dynamic including pulse emissions: in order to evaluate the temporal development of the concentrations or the exposure of a continuous or a pulse emission, also a quasi-dynamic solution is implemented. In line with Brandes et al. (1996), the term 'quasi-dynamic' indicates that all parameters but the chemical concentrations or releases are constant over time. In principle, the user can choose the time step as (s)he likes. However, it must be kept in mind that a time step that is not given in full years is inappropriate when using this climatologically-based model.
- time to reach steady-state: Another temporal feature of WATSON is the so-called 'time to reach steady-state'. This measure indicates how far in the future the steady-state will be reached (e.g., Cowan et al., 1995a; Trapp and Matthies, 1995). Two limits can be defined by the user: the percentage of the steady-state solution and the maximum time period to be investigated. As the time to 100 % steady-state may be in the order of centuries or much longer for metals (e.g., Huijbregts et al., 2001; de Vries et al., 2004) and, thus, converges very slowly, these limits aid to run the computation more efficiently. This third mode of temporal operation comprises the two other modes. An

application of this mode of operation can be found in Bachmann et al. (2004).

For a more general discussion on steady-state and quasi-dynamic modelling as well as their computations for the mathematical approach followed, the reader is referred to sections 2.3.1 and A.1, respectively.

It shall be noted that computations with time steps that are not full years is not adequate in terms of resulting meaningful values for the eventually desired period of time (e.g., seasonal, monthly, daily variations). This is due to the use of long-term average data for the description of the environment.