3 Multimedia environmental fate and/or exposure assessment of prioritised contaminants

The previous Chapter has led to the conclusion that the multimedia modelling approach of the Mackay-type is adopted (cf. Mackay, 1991). In the following, a non-exhaustive review on existing multimedia models of this kind is given in order to evaluate their applicability in the present context. These are at least used for analysing the environmental fate of substances but may comprise also exposure assessment capabilities. As was mentioned before, most of the exposure assessments rely on equilibrium distribution between environmental media and organisms (cf. introduction to section 2.3). Therefore, also some risk assessment schemes are included in the review comprising exposure assessments that follow this concept without utilizing the Mackay environmental fate approach (section 3.1.4).

Due to the fact that there are many different types of substances to which humans might be exposed via soil and water and which require different modelling approaches, a prioritisation of substances is additionally reasoned (section 3.2). Based on this selection and the findings of the model review, the model development needs are formulated (section 3.3).

Before existing modelling approaches are reviewed, it shall be noted that during the development of the present approach another multimedia model for the evaluation of external costs has been proposed (Spadaro and Rabl, 2004). This builds on the generic Uniform World Model (UWM, e.g., Rabl et al., 1998) that was extended by a multimedia exposure assessment (United States - Environmental Protection Agency, 1998). The Uniform World Model only addresses a substance's environmental fate in air which is why it is not relevant in the present context also due to its limited spatial resolution. The followed exposure assessment, in turn, is also presented in section 3.1.4.

3.1 Existing multimedia environmental fate models with or without exposure assessment

Depending on the purpose of an existing multimedia model, one may distinguish between:

- multi-zonal multimedia environmental fate models without exposure assessment,
- multi-zonal multimedia environmental fate and exposure models, and
- oligo-zonal multimedia environmental fate and exposure models.

According to the so-far open questions as regards model design (section 2.3.2), the main evaluation criteria are: geographical scope, spatial differentiation into zones and compartments, exposure assessment capabilities and applicability to the substance types of interest (cf. section 3.2). Further characteristics such as aim and application of the model as well as particularities are also contained in the Tables compiled below.

3.1.1 Multi-zonal multimedia environmental fate models without exposure assessment

There are many spatially-resolved multimedia environmental fate models differing not only with respect to their aim and applicability but also in terms of how the spatial differentiation has been realized (Wania, 1996; Wania and Mackay, 1999; Scheringer and Wania, 2003). Their spatial coverage range from water bodies (Mackay and Southwood, 1992; Wania, 1996; Mackay and Hickie, 2000) over countries (Devillers et al., 1995; Woodfine et al., 2002) to the globe (Wania and Mackay, 1993a, 1995; Scheringer et al., 2000b; Scheringer and Wania, 2003; Wania, 2003). They may comprise the full set of environmental media (i.e., soil, water and air) or just some of them (e.g., water and soil, Di Guardo et al., 1994; Barra et al., 2000). Apart from the 'water body multimedia models' (Mackay and Southwood, 1992; Wania, 1996; Mackay and Hickie, 2000), these models shall be briefly presented here.

There are principally two common criteria for the spatial differentiation of the model's geographical scope into zones. Global models usually follow the latitudes segmenting the globe into climatic bands (Wania and Mackay, 1993a, 1995; Scheringer et al., 2000b; Scheringer and Wania, 2003; Wania, 2003). These are mostly used for the evaluation of the so-called 'cold condensation' or 'global fractionation' theory of Persistent Organic Pollutants (POPs, Wania and Mackay, 1993b; Scheringer et al., 2000b; Scheringer and Wania, 2003; Table 3-1).

The other common criterion when spatially differentiating is according to watersheds (Bintein and Devillers, 1996b; Wania et al., 2000; Woodfine et al., 2001) although some of these authors also take additional criteria into account

Table 3-1: Characteristics of global multi-zonal multimedia environmental fate models without exposure assessment

Characteristics	Globo-POP	Global Multimedia Fate Model
Aim and application	estimation of environmental fate of organic chemicals on the globe that favour enrichment in arctic ecosystems	estimation of environmental fate of organic chemicals on the globe towards the poles; investigating the influence of different numbers of zones
Chemicals considered		
• chemical groups	semi-volatile, non-dissociating, Persistent Organic Pollutants (POPs)	semi-volatile to volatile, non-dissociating, persistent to moderately persistent organic chemicals
• emission to media	emissions into atmosphere, freshwater or cultivated soil	emissions into soil
Environmental fate model		
• type of model	Mackay-type fugacity model	Mackay-type model formulated as a concentration-based mass balance
• temporal scope	steady-state and dynamic (i.e., level III and IV)	steady-state and dynamic (i.e., level III and IV)
• spatial scope and differentiation	the globe is spatially differentiated into 10 latitudinal/meridional bands according to climate	variable amount of latitudinal bands covering the globe
• compartments or media considered	nine bulk compartments: four vertical layers in air, two different types of soil (cultivated and uncultivated), freshwater and freshwater sediments, and the surface ocean	three bulk compartments: soil, oceanic surface water and tropospheric air; limited number for computational efficiency reasons
Remarks on particularities	variable temperatures affecting partitioning	variable temperatures affecting partitioning; variable amount of zones
References	Wania (2003), Wania and Mackay (1995)	Scheringer et al. (2000b)

Table 3-2: Characteristics of a gridded multi-zonal multimedia environmental fate model for Europe (without exposure assessment; Prevedouros et al., 2004)

Characteristics	European gridded model
Aim and application	estimation of environmental fate of Persistent Organic Pollutants (POPs) in the European environment
Chemicals considered	
• chemical groups	Persistent Organic Pollutants (POPs)
• emission to media	at least into the atmosphere
Environmental fate model	
• type of model	Mackay-type fugacity model
• temporal scope	steady-state and dynamic (i.e., level III and IV)
• spatial scope and differentiation	Europe is spatially differentiated into 50 regions according to a 5 x 5 degree grid plus four perimetric boxes (i.e., the Atlantic, Mediterranean, Eurasian and Arctic box)
• compartments or media considered	seven bulk compartments: upper and lower atmosphere, soil, vegetation, freshwater and sediment, and coastal water
Remarks on particularities	-
References	Prevedouros et al. (2004) building on BETR North America (cf. Table 3-3)

(Table 3-3). These include climatic and ecological characteristics (Bintein and Devillers, 1996b), and biophysical geographic (temperature, precipitation, ecosystem type, soil type, land use and meteorology), social geographic (population distribution, industrial and agricultural activity) and political factors (Woodfine et al., 2001) among other, although basically only soil types seem to play a role for the delineation of the BETR North America model apart from watershed information (MacLeod et al., 2001).

Recently, a gridded multimedia Mackay model has been published (Prevedouros et al., 2004, Table 3-2). It subdivides Europe into 50 regions according to a 5 x 5 degree grid surrounded by four boxes. Water connectivities in the terrestrial environment were defined based on river discharge information.

Many of the purely environmental fate models just presented are designed to analyse the behaviour of non-ionizing, organic substances belonging to the group of Persistent Organic Pollutants (POPs). Due to their persistency, POPs may show rather long residence times in air which bring about a long-range transport potential. Therefore, several of these models at least distinguish two atmospheric layers (Wania and Mackay, 1995; MacLeod et al., 2001; Wania, 2003; Prevedouros et al., 2004).

The POPCYCLING-Baltic model (Wania et al., 2000) is special in mainly two respects. First, it shows a different spatial differentiation of the air environment from the terrestrial/marine environment. Secondly, it computes not only mass balances for the substance under investigation but also for the carrier phases air, water and particulate organic carbon in water. Furthermore, it considers sediments in the marine environment and distinguishes between coastal zones and open sea. In the case of the Baltic Sea, the term 'open sea', however, must be seen relatively.

3.1.2 Multi-zonal multimedia environmental fate and exposure models

There are only a few multi-zonal multimedia environmental fate and exposure models available at present. The main one encountered which is relevant here is IMPACT 2002 (Pennington et al., 2005; Jolliet et al., 2003). Its characteristics are presented in Table 3-4.

IMPACT 2002 comprises large parts of Europe, i.e., most of Western Europe. Similar to the POPCYCLING-Baltic model (Wania et al., 2000), it follows different delineation schemes for air and the terrestrial environment. According to a master's thesis related to the development of IMPACT 2002 (Pelichet, 2003), a segmentation of the atmosphere following irregular boundaries such as watersheds introduces errors especially when the substance to be investigated is rather short-lived in air. Therefore, a delineation of the atmosphere according to a grid is suggested which is in line with many existing air quality models for larger scales (Pekar et al., 1999; Green et al., 2000; Bey et al., 2001; Ilyin et al., 2001), global water balance models (e.g., Vörösmarty et al., 1998) and also with the European gridded model presented above (Table 3-2). While the sea environment also follows the grid delineation for air, the terrestrial environment is spatially differentiated in IMPACT 2002 according to watersheds.

Unlike the environmental fate models presented in section 3.1.1, IMPACT 2002 provides full exposure and impact assessment capabilities (Pennington et al., 2005; Jolliet et al., 2003). For human health, different exposure pathways are aggregated into the so-called Intake Fraction (Bennett et al., 2002) which assesses the portion of an emission that a population will be finally exposed to. By aggregating the exposure at the population level, a so-called 'production-

Table 3-3: Characteristics of multi-zonal multimedia environmental fate models applicable to particular regions of the world

Characteristics	CHEMFRANCE	BETR North America[a]	POPCYCLING-Baltic
Aim and application	estimation of environmental fate of organic chemicals in France	evaluating long-range transport potential of organic pollutants; formulation of continent-scale management and regulatory strategies for chemicals	non-steady state multimedia mass balance model for assessing long term fate of persistent organic pollutants (POPs) in the Baltic Sea environment
Chemicals considered			
• chemical groups	organic chemicals that may also dissociate[b]	organic pollutants	semi-volatile, non-dissociating, persistent organic chemicals (POPs)
• emission to media	emissions to air, water, soil and sediment	(not specified)	emissions to air, forest canopy[c], forest soil, agricultural soil, freshwater and coastal water
Environmental fate model			
• type of model	Mackay-type fugacity model	Mackay-type fugacity model	Mackay-type fugacity model
• temporal scope	steady-state (level III) if one region is investigated; or seasonal results for the whole modelled area (i.e., France)	steady-state and dynamic (i.e., level III and IV)	dynamic (i.e., level IV)

Table 3-3: Characteristics of multi-zonal multimedia environmental fate models applicable to particular regions of the world

Characteristics	CHEMFRANCE	BETR North America[a]	POPCYCLING-Baltic
• spatial scope and differentiation	France is differentiated into 12 regions according to hydrological (drainage basins), climatic (precipitation, temperature, wind) and ecological criteria (nature of soil and vegetation type)	the North American Continent consisting of Canada, the United States of America and Mexico is subdivided into 24 regions principally according to watersheds and soil types	the model's scope is differentiated differently for the terrestrial and sea environment (following mostly the eight aquatic sub-basins of the Baltic Sea and related drainage areas), and air (four air-sheds)
• compartments or media considered	six bulk compartments: air, fresh surface water (including fish), soil, sediment of freshwater bodies, ground water, coastal water	seven bulk compartments: two air layers, vegetation, soil, freshwater and sediment, and coastal water	ten bulk compartments: air, agricultural soil, forest soil and canopy, freshwater and sediment, coastal water and sediment, and open sea water and sediment
Remarks on particularities	dissociating organic substance can be modelled[b]	emission rates and temperatures may be allowed to vary in time	advective intercompartmental transfer fluxes of the contaminants are calculated as the product of a flux of a carrier phase (air, water and particulate organic carbon) and a contaminant concentration in that phase; mass balances calculated for carrier phase; forest canopy distinguished as a compartment; different spatial resolutions for air and the other media

Table 3-3: Characteristics of multi-zonal multimedia environmental fate models applicable to particular regions of the world

Characteristics	CHEMFRANCE	BETR North America[a]	POPCYCLING-Baltic
References	Devillers et al. (1995), Bintein and Devillers (1996b), Bintein and Devillers (1996a)	Woodfine et al. (2001), MacLeod et al. (2001)	Wania et al. (2000)

a. The latest version of ChemCAN (Woodfine et al., 2002) appears to build mostly on the BETR North America model which in turn is an expansion of an earlier version of ChemCAN (MacLeod et al., 2001, p. 2); it just has a smaller geographical scope while keeping 24 distinguished zones.

b. A pH dependency of possible ionization in fresh surface water and its sediment can be considered as was done by Bintein and Devillers (1996b).

c. The author is irritated as to how emissions directly into the leaves/needles in a forest canopy can actually be mediated/accomplished (cf. p. 44, ibid.).

Table 3-4: Characteristics of IMPACT 2002, a multi-zonal multimedia environmental fate and exposure model

Characteristics	IMPACT 2002
Aim and application	estimation of environmental fate and related effects of mostly organic chemicals in Western Europe
Chemicals considered	
• chemical groups	organic chemicals, metals
• emission to media	emissions to air, water and soil
Environmental fate model	
• type of model	Mackay-type model formulated as a mass-based mass balance
• temporal scope	steady-state and dynamic (i.e., level III and IV)
• spatial scope and differentiation	Western Europe is spatially differentiated and contained in a global box; spatial differentiation of the terrestrial environment according to drainage basins into 135 zones; air is spatially differentiated according to a 2 x 2.5 degree grid; oceanic zones follow the air grid where applicable
• compartments or media considered	seven bulk compartments: air, fresh surface water and related sediment, agricultural and natural soil, oceanic water and related sediment
Exposure model	
• target / safeguard organisms	human health, and aquatic and terrestrial ecosystems
• routes considered	inhalation and various ingestion pathways
Effect / impact model	human health: cancer and non-cancer effects considered following the Disability Adjusted Life Years (DALY) concept (Murray and Lopez, 1996a, 1996b); aquatic and terrestrial ecosystems: potentially affected fraction
Remarks on particularities	different spatial resolutions for air/sea and soil/freshwater; 'production-based' exposure assessment; different exposure pathways aggregated into the Intake Fraction (Bennett et al., 2002)
References	Jolliet et al. (2003), Pennington et al. (2005)

based' approach is realized (Pennington et al., 2005) which accounts for the division of labour and overcomes the conservative 'subsistence farmer' approach mostly followed by screening regulatory risk assessments. The effects on human health due to the estimated exposure is assessed following the Disability Adjusted Life Years (DALY) concept (Murray and Lopez, 1996a, 1996b).

Another example is the Total Risk Integrated Methodology (TRIM, United States - Environmental Protection Agency, 1999a, 1999b, 2002a, 2002b) . The TRIM design offers a rather flexible framework for the assessment of so-called hazardous and criteria air pollutants, examples for the latter are particulate matter, ozone, carbon monoxide, nitrogen oxides, sulphur dioxide and lead (United States - Environmental Protection Agency, 1999b). The flexibility is realized, for instance, by the capability of using different environmental fate models that may be based on first-order or higher order algorithms (United States - Environmental Protection Agency, 2002b). While aiming at multimedia capabilities, the modular design may even allow to use single medium models (e.g., Gaussian plume models for air, United States - Environmental Protection Agency, 1999b). It is still being developed which is why only a few of the components principally aimed at are ready for use. In the case of the fate module, only first-order models are available (United States - Environmental Protection Agency, 2002a). Also only inhalation exposures can be assessed at present. Due to its preliminary status and its principally flexible design, it is not further presented here.

The Framework for Risk Analysis in Multimedia Environmental Systems (FRAMES) is a third example of this type of models (Whelan et al., 1997). Similar to TRIM, however, it allows for the inclusion and combination of different models. Therefore, its characteristics are not well determined which is why it will not be analysed here either, noting that modularity and flexibility in terms of combinations of different models offers well-suited, task-specific assessment capabilities.

3.1.3 Oligo-zonal multimedia environmental fate and exposure models

Oligo-zonal multimedia environmental fate and exposure models shall be reviewed next. By 'oligo-zonal', it is meant that the geographical area of prime interest is not further subdivided into zones although noting that in the case of nesting different hierarchical levels may be taken into account.

All of the models presented in Table 3-5 combine at least in parts a Mackay-type multimedia model with an exposure and risk assessment (McKone, 1993a, 1993b; Brandes et al., 1996; European Commission, 1996a; Vermeire et al., 1997; Schwartz et al., 1998; Schwartz, 2000; Huijbregts, 1999, 2000; Huij-

Table 3-5: Characteristics of oligo-zonal multimedia environmental fate and exposure models

Characteristics	CalTOX	EUSES	USES-LCA	Dynabox
Aim and application	assist in health-risk assessments that address contaminated soils and the contamination of adjacent air, surface water, sediments and ground water	screening and refined quantitative risk assessment of the risks posed by new and existing chemical substances to man and the environment	performing Life Cycle Impact Assessment of toxic substances at the global scale	performing dynamic risk assessments of metals
Chemicals considered				
• chemical groups	mostly non-ionic organic chemicals, also ionic organic and inorganic chemicals such as metals	mostly non-ionic organic chemicals	mostly non-ionic organic chemicals, also ionic organic and inorganic chemicals such as metals	metals
• emission to media	originally emissions to soil ("soil-bound contaminants" McKone, 1993b, p. 8) but allowing for inputs to any of the distinguished compartments	locally: air and water; regionally and continentally: air, industrial soil, sewage treatment plant and water	emissions into air, freshwater, sea water, and agricultural and industrial soil	(not specified)

Table 3-5: Characteristics of oligo-zonal multimedia environmental fate and exposure models

Characteristics	CalTOX	EUSES	USES-LCA	Dynabox
Environmental fate model				
• type of model	Mackay-type fugacity model	local scale: different models for air, sewage treatment plant, surface water and soil; regional and continental scale: Mackay-type model formulated as a concentration-based mass balance[a]	Mackay-type model formulated as a concentration-based mass balance[a]	Mackay-type model formulated as a concentration-based mass balance[a]
• temporal scope	steady-state and dynamic (i.e., level III and IV)	regional and continental scale: steady-state (i.e., level III)	steady-state and dynamic (i.e., level III and IV)	steady-state and dynamic (i.e., level III and IV)
• spatial scope and differentiation	regional, no (lateral) differentiation	generic or standard environment (may be adapted); three nested scales, i.e., local, regional, continental, plus a personal scale (only exposure assessment)	global; two nested scales, i.e., continental and global; global scale is differentiated into three climate zones (arctic, moderate, tropic)	global; three nested scales, i.e., regional, continental and 'outside' world

Table 3-5: Characteristics of oligo-zonal multimedia environmental fate and exposure models

Characteristics	CalTOX	EUSES	USES-LCA	Dynabox
• compartments or media considered	seven bulk compartments: air, ground-surface soil, root-zone soil, vadose-zone soil, plants, surface water and sediment	local: depending on the model employed; regional and continental (six bulk compartments): air, water, sediment, and natural, agricultural and industrial soil	continental (eight bulk compartments): air, freshwater and sediment, sea water and sediment, and natural, agricultural and industrial soil; global (three bulk compartments): air, sea water, soil	regional: air, surface water, suspended matter, biota, sediment, natural soil, agricultural sand soil, agricultural peat soil, agricultural clay soil, pore water in sand soil, pore water in peat soil, pore water in clay soil, industrial soil, ground water; continental: air, surface water, suspended matter, biota, sediment, natural soil, agricultural soil, industrial soil, ground water; sea: air, sea water, suspended matter, biota, sediment; outside world: deep soil, deep sediment

Table 3-5: Characteristics of oligo-zonal multimedia environmental fate and exposure models

Characteristics	CalTOX	EUSES	USES-LCA	Dynabox
Exposure model				
• target / safe-guard organisms	human health	man: consumers, workers and man exposed through the environment; environment: sewage treatment plant populations of micro-organisms, aquatic, terrestrial and sediment ecosystems, and populations of predators	human health and environment distinguished into freshwater aquatic and sediment, sea water aquatic and sediment, and terrestrial environment	human health, and aquatic and terrestrial ecosystems
• routes considered	inhalation and various ingestion pathways (total of 23 different exposure pathways); aggregated into an average daily potential doses	man: inhalation, ingestion of food (i.e., fish, root crops, leaf crops, meat, milk) and drinking water, exposure towards consumer products and at the workplace; environment: water - fish - predators, soil - earthworm - predators	inhalation and ingestion including soil ingestion for humans; other organisms via contact with the environmental medium	(not explicitly stated)

Table 3-5: Characteristics of oligo-zonal multimedia environmental fate and exposure models

Characteristics	CalTOX	EUSES	USES-LCA	Dynabox
Effect / impact model	Human Toxicity Potentials (HTPs); based on Risk Characterisation Ratios (RCRs) relating potential dose to a measure of inherent toxicity; HTPs are the ratio of a substance's RCR and another of a reference substance; given for cancer and non-cancer effects	Risk Characterisation Ratio: man: Margin of Safety (MOS); environment: PEC/PNEC ratio	toxicity potentials based on normalized Risk Characterisation Ratios (RCRs): man: predicted daily intakes related to so-called human limit values for humans; else: PEC/PNEC ratios	Risk Characterisation Ratios (RCRs): man: predicted daily intake related to so-called Acceptable Daily Intake (ADI); else: PEC/PNEC ratios

Table 3-5: Characteristics of oligo-zonal multimedia environmental fate and exposure models

Characteristics	CalTOX	EUSES	USES-LCA	Dynabox
Remarks on particularities	vertical differentiation of the soil compartment into layers; contaminant concentrations in ground water are based on the leachate from the vadose-zone soil; uncertainty and sensitivity analysis capabilities	conservative ('reasonable worst case'), screening level; release scenarios provided; sewage treatment plant; local scale; different risk characterisation (i.e., based on acute or chronic data) depending on whether intermittent or continuous releases are considered; several features of SimpleBox 2.0 (Brandes et al., 1996) are not used in EUSES: global spatial scope by means of a moderate, an arctic and a tropic zone, variable soil depth, vegetation compartment, fish as part of suspended solids, performing a temperature correction and computing dynamically	almost closed system due to global spatial scope except for exchange with the stratosphere; worst-case estimates are replaced by realistic ones; chemical-specific penetration depths into soils; temperature dependency of hydroxyl-radical reaction rates as well as influence of pH on environmental behaviour of dissociating substances and hydrolysis rates considered	'outside' world provides only ultimate sinks; "The differentiation of agricultural soil into sand, peat and clay does not affect the overall picture. However, it introduces differences in soil concentrations of a factor up to 10." (Heijungs, 2000, p. 75)

Table 3-5: Characteristics of oligo-zonal multimedia environmental fate and exposure models

Characteristics	CalTOX	EUSES	USES-LCA	Dynabox
References	McKone (1993a), McKone (1993b), McKone and Hertwich (2001), Hertwich (1999), Hertwich et al. (2001)	Brandes et al. (1996), European Commission (1996a), Vermeire et al. (1997), Schwartz et al. (1998), Schwartz (2000)	Huijbregts (1999), Huijbregts (2000), Huijbregts et al. (2000a), Huijbregts et al. (2000b), Huijbregts et al. (2001)	Heijungs (2000)

a. The environmental fate model builds on SimpleBox (e.g., Brandes et al., 1996). The mass balance of this model is based on concentrations and not on fugacities.

bregts et al., 2000a, 2000b, 2001; Heijungs, 2000; McKone and Hertwich, 2001). Their substance coverage is mostly non-ionic organic chemicals although CalTOX (McKone, 1993b) and USES-LCA (Huijbregts et al., 2000b) also have been applied for other substances such as metals. Dynabox was explicitly developed for the application to metals (Heijungs, 2000). In order to better model dissociating substances and hydrolysis, USES-LCA introduced compartment-specific pH values (Huijbregts, 1999). Fugacity-based environmental fate model formulations are principally designed to address rather volatile substances. In order to also assess rather involatile substances, a so-called 'aquivalence approach' was developed (Mackay and Diamond, 1989) which is included in the CalTOX model. In contrast to CalTOX, the other tools show nesting of different spatial scales, thereby reaching continental (European Commission, 1996a; Heijungs, 2000) or even global coverage (Huijbregts et al., 2000b). In terms of spatial differentiation into compartments, a special feature of CalTOX is that it distinguishes three different layers in soil, a feature that was largely supported by recent findings as regards volatile organic compounds (McKone and Bennett, 2003). Dynabox, in turn, differentiates different types of agricultural soil which however "does not affect the overall picture" (Heijungs, 2000, p. 75) and also adds an outside world with a deep soil and deep sediment compartment as ultimate sinks.

CalTOX probably constitutes one of the most comprehensive models to address human exposures covering a total of 23 different exposure pathways (McKone, 1993a; McKone and Enoch, 2002). The other approaches are not as comprehensive with respect to human health noting that EUSES also assesses exposures at the work-place and via consumer products. EUSES, USES-LCA and Dynabox, however, additionally assess exposures of other safeguard objects such as terrestrial and aquatic ecosystems.

All effect assessments follow risk characterisation approaches relating an environmental medium concentration to a safe concentration such as the PEC/PNEC ratio or a dose to which an individual may be exposed to a safe dose. These are called Risk Characterisation Ratios (RCRs). In case of human health risk assessment, EUSES makes use of the Margin Of Safety (MOS, European Commission, 1996a) concept which simply relates a safe dose to the estimated exposure dose. The risk assessor might then judge whether the resulting MOS is large, i.e., protective enough or not. The Human Toxicity Potentials (HTPs) assessed by CalTOX (Hertwich, 1999; Hertwich et al., 2001; McKone and Hertwich, 2001) are based on RCRs relating a potential dose to a measure of inherent toxicity such as cancer potency and Reference Dose (RfD) or Reference Concentration (RfC) for cancer and non-cancer effects, respectively (Hertwich et al., 2001). The HTPs are yielded by dividing the RCR of a substance under study by one of a reference substance (normalization) both obtained from the same emission scenario. The toxicity potentials as used by USES-LCA are computed analogously for all safeguard objects (Huijbregts et al., 2000b). All these risk characterisations constitute threshold approaches indicating whether there is concern or not. In particular when used at screening level, EUSES is meant to be conservative (European Commission, 1996a), i.e., rather overestimating than underestimating a risk.

3.1.4 Non-Mackay-type multimedia environmental fate and exposure assessment frameworks

In this section, exposure assessment approaches and tools are presented that do not build on Mackay-type environmental fate models. Due to the usual modularity employed in the risk assessment, the exposure assessment parts can, nevertheless, be combined with the results of other types of environmental fate models. Principally, two exposure assessment tools with multimedia capabilities and applicable to trace elements (cf. section 3.2) have been encountered in the literature that have not yet been presented here: One is from the health physics (radionuclides) context suggested by the International Atomic Energy Agency (2001) and the other applies to hazardous air contaminants (United States - Environmental Protection Agency, 1998). It shall be noted that there may be other assessment frameworks and tools available not reviewed or even mentioned here.

The environmental fate models that are also provided by these assessment frameworks are detailed in Table 3-6. Most notably, the Human Health Risk Assessment Protocol (HHRAP) is intended to provide guidance for location-specific analyses of emissions to air from hazardous waste combustion facilities (United States - Environmental Protection Agency, 1998) whereas the framework suggested by the IAEA is generic concentrating on radionuclides (International Atomic Energy Agency, 2001).

Only the related exposure and risk assessment parts of these approaches shall be presented in the following. Due to the nature of the investigated substances, the simple safety assessment models for radionuclides not only include the inhalation and ingestion routes of exposure but also *external exposure* (International Atomic Energy Agency, 2001), i.e., the exposure due to staying in the vicinity of contaminated environmental media. Such induced effects due to 'remote' exposure are a particularity of radioactive substances. While both approaches cover inhalation and ingestion exposures, the degree of detail by which the HHRAP assesses ingestion is higher (United States - Environmental Protection Agency, 1998). The HHRAP takes more exposure pathways into account by distinguishing between different vegetal produces (i.e., belowground, aboveground protected and aboveground exposed produce) and including more animal produces such as poultry, eggs and pork.

Table 3-6: Characteristics of multimedia exposure approaches for trace elements/radionuclides

Characteristics	Simple safety assessment models by IAEA	Human Health Risk Assessment Protocol (HHRAP)
Aim and application	providing simple methods for calculating doses arising from radioactive discharges into the environment	providing guidance for performing risk assessments of substances being released by hazardous waste combustion units
Chemicals considered		
• chemical groups	radionuclides	hazardous organic chemicals and trace elements, so-called 'compounds of potential concern' (COPCs)
• emission to media	continuous or prolonged emissions from small scale facilities to air, water and sewage systems	emissions to air excluding accidental releases
Environmental fate model		
• type of model	first stage: 'no dilution model'; second stage: simple generic environmental models for air (Gaussian plume model), water (depending on the water body) and soil (based on atmospheric deposition and removal rates, e.g., due to decay)	different models for different media: air: Industrial Source Complex Short-Term Model (ISCST3); soil: based on atmospheric emission or deposition and removal rates, e.g., due to degradation or physical removal; water: based on atmospheric deposition, inputs from land and removal rates
• temporal scope	equilibrium conditions	equilibrium conditions

Table 3-6: Characteristics of multimedia exposure approaches for trace elements/radionuclides

Characteristics	Simple safety assessment models by IAEA	Human Health Risk Assessment Protocol (HHRAP)
• spatial scope and differentiation	generic; no differentiation	location-specific (close to a hazardous waste incinerator); no differentiation
• compartments or media considered	air, water (rivers, estuaries, coastal waters, lakes and reservoirs); soil only as part of the terrestrial food chain (derived from atmospheric deposition)	mostly air based on which other media concentrations are derived
Exposure model		
• target / safeguard organisms	human health	human health
• routes considered	inhalation (air and resuspended solids), ingestion (plants, milk, meat, fish, drinking water, and soil particles by animals and humans) and external exposure (e.g., when staying in or at radionuclides containing air, sediments etc.)	inhalation and ingestion of belowground and aboveground (protected and/or exposed) produce, beef and dairy products, pork, chicken and eggs, drinking water, and fish; note: no inhalation and drinking water exposures of farm animals considered
Effect / impact model	collective dose compared to reference level	Risk characterisation: cancer: based on slope factor and lifetime average daily dose; non-cancer: hazard quotient relating either average daily dose to the Reference Dose (RfD) or air concentration to the Reference Concentration (RfC)

Table 3-6: Characteristics of multimedia exposure approaches for trace elements/radionuclides

Characteristics	Simple safety assessment models by IAEA	Human Health Risk Assessment Protocol (HHRAP)
Remarks on particularities	conservative, screening level; assuming (quasi-) equilibrium conditions between released radionuclides and the environment	higher tier approach than screening level ("reasonable potential risk", p. 1-6), less conservative than the latter
References	International Atomic Energy Agency (2001)	United States - Environmental Protection Agency (1998)

Similar to the approaches presented in the previous section 3.1.3, both effect assessments make use of Risk Characterisation Ratios (RCRs). It is noted that the HHRAP also distinguishes between cancer and non-cancer effects similar to CalTOX (Hertwich et al., 2001). While the approach suggested by the IAEA is meant for screening level assessments (International Atomic Energy Agency, 2001) and, thus, rather overestimating than underestimating exposures and/or effects, the HHRAP is location-specific and tries to evaluate reasonable rather than theoretical worst-case maximum potential risks (United States - Environmental Protection Agency, 1998).

3.2 Selection of contaminants

Before drawing conclusions with respect to the development needs (cf. section 3.3), the scope of the substances to be covered shall be defined. It was argued in section 2.3.2 that a rather simple mathematical framework is adopted due to the spatial scale at which the model shall operate and related data availability constraints. The framework follows the multimedia type of modelling, as first suggested by Mackay (Mackay, 1979, 1991).

It is more than obvious that depending on the questions to be answered different prioritisations of substances will result. For instance, when providing decision support for the ban of substances (cf. Stockholm convention on Persistent Organic Pollutants, POPs) only substances whose production is not yet banned is of relevance. For the assessment of the welfare of societies, on the contrary, also impacts due to such banned substances need to be included in the evaluation if they still lead to impacts (European Commission, 2003d). Another example is burning wood in open fire places which may substantially contribute to a person's exposure towards particulate matter. However, this (indoor) exposure is irrelevant in terms of external cost assessments as the related costs need to be classified as internal, assuming that the person burning the wood is aware of the consequences in terms of health effects. Also the scale at which the analysis will be performed will guide the selection of sources to be considered (Reimann et al., 2000).[5]

The present work aims at elaborating and providing a methodology for the assessment of external costs due to multimedia exposures, thereby extending an existing approach for inhalation exposures (European Commission, 1999a). As a consequence, one of the main aims of the case studies to be presented in

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[5] "(O)n a regional scale mobile pollution sources such as traffic or industrial activities using large tracts of land such as agriculture and forestry may have a considerably stronger impact on environmental quality than local industrial pollution sources" (ibid., p. 168).

Chapters 10 and 11 is to demonstrate the application of the suggested approach. As there are some hundreds or even thousands of substances that may be hazardous, a limitation in the initial coverage of the model to be developed with respect to substances is necessary especially due to resource constraints.

The most important selection criterion is *relevance* for which political concern is taken as a proxy. There is public concern about long-lived substances such as heavy metals and POPs due to accumulation in the environment (e.g., Lindberg, 1989; Kabata-Pendias and Pendias, 1992; United Nations - Economic Commission for Europe, 1998; Rat von Sachverständigen für Umweltfragen, 2004) that are furthermore either poisonous or bioaccumulative or both. Such substances have influenced many legislation processes and policy initiatives for instance at the European Union level such as the Water Framework Directive (WFD, 2000/60/EC, Parliament and Council of the European Union, 2000), the preparation of the fourth Daughter Directive for the Air Quality Framework Directive (AQFD, 96/62/EC, Council of the European Union, 1996b), the Integrated Pollution Prevention and Control Directive (IPPC, 96/61/EC, Council of the European Union, 1996a), the European Environment and Health Strategy (European Commission, 2003f) and the EU Thematic Strategy on Soil (European Commission, 2003g) to name some of them. Recent evidence suggests that metal contamination via air is of high actuality in that the highest atmospheric depositions into Alpine glaciers occurred in the second half of the twentieth century since the mid seventeenth century (Barbante et al., 2004).

The project series Externalities of Energy (ExternE) has focused on external costs resulting directly or indirectly from energy conversion techniques (European Commission, 1999a). Since the present work builds on the ExternE-methodology, another selection criterion is to include only those substances in the assessment that are predominantly emitted by energy conversion techniques. A fairly recent study by the United States Environmental Protection Agency (US-EPA, French et al., 1998) quantifies the impacts of fossil fuelled power plants in the USA, thus providing valuable guidance on priorities for the analysis. The highest priority is given to mercury, followed by arsenic and by dioxins and furans. Lead, cadmium, chromium and nickel are also studied in detail but found to be less important than mercury and arsenic. In fact, US-EPA considers that lead and cadmium are not priorities. However, for lead there is a significant difference between the USA and Europe due to background exposures since in the USA leaded gasoline was phased out 10 to 20 years earlier; furthermore, even so-called unleaded gasoline contains some lead, currently about 10 % of leaded gasoline, to be reduced in future years.

3.2.1 Discussion on mercury and its compounds

The assessment of mercury is rather demanding. Mercury occurs predominantly in the gaseous phase in the atmosphere (Puxbaum, 1991) of which a lower bound share of 95 % is elemental mercury according to Fitzgerald (1994) cited in United States - Environmental Protection Agency (1997b). Due to the long residence time of elemental mercury in air (in the order of months to years, Lindqvist and Rodhe, 1985; United States - Environmental Protection Agency, 1997b), the air quality modelling should not be confined to the atmospheric boundary layer and should at least cover one hemisphere if not the globe (United States - Environmental Protection Agency, 1997b; Ryaboshapko et al., 1998) similar to many Persistent Organic Pollutants (Pekar et al., 1999). Furthermore, several species are involved. Three species may be differentiated for regional air quality purposes: elemental mercury (Hg0), divalent mercury (HgII) and particulate-bound mercury (e.g., Ryaboshapko et al., 1998 and RELMAP as described by United States - Environmental Protection Agency, 1997b). The model by EMEP additionally considers methyl mercury (MHg, Ryaboshapko et al., 1998) with a relatively short atmospheric half-life of 12 hours due to ready photochemical and chemical degradation. As methyl mercury usually only constitutes a minor fraction of the overall mercury in air, there is good reason to exclude it from air quality modelling exercises. In particular when modelling water and/or wetlands (e.g Olson and Panigrahi, 1991; United States - Environmental Protection Agency, 1997b), however, this species gains in importance and needs to be explicitly considered due to its potential toxic effects (cf. Tsiros, 2001 and model 'IEM-2M', United States - Environmental Protection Agency, 1997b). The consideration of different species and more importantly the confined spatial coverage of the existing external cost assessment tool EcoSense make the inclusion of mercury meaningless since especially the intercontinental air transport cannot be modelled appropriately. As a result, mercury is not included in the present analysis.

3.2.2 Discussion on 'dioxins'

As stated above, the US-EPA also identified dioxins as priority substances (French et al., 1998). The term 'dioxins' usually refers to a group of polychlorinated, planar aromatic compounds with similar structures, and chemical and physical properties (Anonymous, 2000). Each of these compounds is also referred to as *congener*. This group of compounds consists of 75 polychlorinated dibenzo-*p*-dioxins (PCDDs) and 135 polychlorinated dibenzofurans (PCDFs), of which 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin (TCDD) is the most toxic and most studied congener. Dioxins are lipophilic compounds that bind to sediment and organic matter in the environment and tend to be absorbed in animal and human fatty tissue. The seventeen 2,3,7,8-chlorine substituted PCDD and PCDF congeners in particular are extremely resistant towards chemical and biological degradation processes and, consequently, persist in the environment and accumulate in the food chain. There is evidence that the so-called coplanar polychlorinated biphenyl (PCB) congeners exert a similar effect on living organisms like PCDDs and PCDFs. The group of PCBs is, therefore, also counted to the 'dioxins'. It consists of 209 congeners of which 130 are likely to occur in commercial products (Anonymous, 2000) which is in contrast to the dioxins and furans which have never been produced intentionally. PCDD/Fs and PCBs belong to the group of POPs which are internationally banned according to the Stockholm convention on Persistent Organic Pollutants noting that the usage of POPs that are active ingredients of pesticides is still allowed in some countries.

As PCDD/Fs and PCBs are normally present in environmental and food samples as complex mixtures of congeners causing comparable effects, the concept of Toxic Equivalents (TEQs) has been developed. This concept uses the available toxicological and biological data to generate a series of weighting factors, called Toxic Equivalency Factors (TEFs), each of which expresses the toxicity of a 'dioxin-like' compound in terms of the equivalent amount of the most toxic dioxin congener, 2,3,7,8-TCDD (Harrison, 2001b). Multiplication of the concentration of a compound by its TEF yields a TEQ. Also the exposure-response information for ingested dioxins is given per TEQ (United States - Environmental Protection Agency, 2001) based on the World Health Organisation Toxic Equivalency Factors (WHO-TEFs, van den Berg et al., 1998) superseding a former set of so-called International Toxic Equivalency Factors (I-TEFs, North Atlantic Treaty Organization/Committee on the Challenges of Modern Society, 1988).

Apart from exposure through accidents and at the working environment, human exposure to dioxins is mostly attributable to ingestion (more than 90 %, Buckley-Golder et al., 1999; Fiedler et al., 2000; European Commission, 2001b). Hence, contaminated plants and animals that are eaten need to have become exposed prior to human exposure. Contamination of the environment with dioxins is primarily caused by the aerial transportation and deposition of emissions from various sources although dioxins with natural origin might also enter the food chain via cattle feed (Ferrario et al., 2000). In principle, plants may also accumulate pollutants via root uptake from the soil but the importance of the soil-to-plant pathway for dioxins is generally negligible (Welsch-Pausch et al., 1995; Wania and Mackay, 1999; Cousins and Mackay, 2001) and confined with respect to plant species (McLachlan, 1997).

Another possible exposure pathway may be due to sludge 'amendments' to soils. The exposure from sludge to plant into the food chain is of minor importance and depends on the level of sludge contamination, the intensity of sludge use and the agricultural practices (McLachlan et al., 1996). In Germany, sludge amendments to grassland are even prohibited (Fiedler, 2003) and food items are treated prior to consumption.

In order to allow for attributing an exposure to an emission of dioxins by a human activity (i.e., the impact pathway), in principle chemical transport models would need to be applied for each of the PCDD, PCDF and PCB congeners. Although the exposure-response information is given in an aggregated way, a differentiated modelling approach is necessary due to the fact that the congeners contributing to the toxic effects show very different dispersion behaviours in the atmosphere (Eitzer and Hites, 1989; Kaupp et al., 1994; Oh et al., 2001) with octachlorinated dibenzo-*p*-dioxin (OCDD) possibly even being built from pentachlorophenol (PCP, e.g., Baker and Hites, 2000). Additionally, it is known that vegetation considerably influences the atmospheric transport of dioxins (Bennett et al., 1998; McLachlan and Horstmann, 1998; Cousins and Mackay, 2001). Consequently, an air dispersion model considering exchange processes with vegetation is needed for the assessment of dioxins not only for inhalation but also for a considerable portion of the ingestion exposures. This is because root uptake is generally negligible (Welsch-Pausch et al., 1995; Cousins and Mackay, 2001) and the contribution of fish for instance ranges from 2 % to 63 % across the European Union depending on the consumption habits of a (sub-) population according to Anonymous (2000). Most of the fish consumed in the EU stems from sea catches (European Centre for Ecotoxicology and Toxicology of Chemicals, 1994), however, which would bring about the need to model the fate of the assessed substances also in the marine environment which is not attempted in the present study (cf. section 6.1). As a result, the necessary air quality model that includes vegetation has not been available which is why a comprehensive external cost assessment due to ingestion of dioxins remains open.

3.2.3 Trace elements and Mackay modelling

The remaining substances considered in the US-EPA report are first of all arsenic and secondly heavy metals such as cadmium and lead (French et al., 1998). Although it was concluded in that study that for example cadmium and lead are not priorities, this must be seen from a regulatory risk assessment perspective where exposure levels are compared to safe levels. While this approach is valid, for instance, when trying to protect the most exposed individual, the assessment of external costs due to effects at the population level supports the assumption that there is no safe level, i.e., that there is no effect threshold (cf. section 7.3). From an external cost point of view, hence, there is concern about each substance that has the potential to cause adverse effects.

In order to estimate external costs based on adverse effects following ingestion, corresponding dose- or exposure-response functions are required. Exposure-response information for ingestion is very scarce (cf. Searl, 2002). In order to derive slope factors from threshold information, a method has been proposed fairly recently which is adopted in this study (Crettaz, 2000; Crettaz et al., 2002; Pennington et al., 2002; cf. section 7.3.1), offering the possibility to assess not only inorganic arsenic for which exposure-response information is available only via drinking water (e.g., United States - Environmental Protection Agency, 2005) but also heavy metals such as cadmium, lead and hexavalent chromium. Note that, although arsenic as a metalloid strictly speaking does not belong to the group of heavy metals, it is common use in the scientific and the regulatory literature to consider arsenic part of the (heavy) metals (e.g., Pacyna, 1987; Berdowski et al., 1997; Buse et al., 2003; European Commission, 2003f, 2003g; Joint Research Centre of the European Commission, 2003). It may be more appropriate to call these elements *trace elements* altogether since their occurrence in the 'experienced' environment, i.e., at the earth's surface, is limited (Wedepohl, 1991, 1995).

Heavy metals including arsenic is a group that has been widely disregarded (or rather avoided) in the realm of Mackay-type multimedia modelling, one reason being that heavy metals need individual treatment (Mackay, 1991; Hertwich et al., 2000). Examples of multimedia models that were applied to heavy metals are USES-LCA (Huijbregts et al., 2000a, 2000b), the EQC (only lead, Mackay et al., 1996a) and CalTOX (e.g., Hertwich et al., 2000). As pointed out by several authors, research in multimedia modelling of metals is, however, needed (Hertwich et al., 2000; Huijbregts et al., 2001).

It is assumed here that heavy metals except for mercury do not have a significant vapour pressure so that they can be considered to be non-volatile (Lide, 2002). Due to this characteristic, multimedia models that are based on fugacity face the problem to deal with this group of substances. This is why the aquivalence approach has been introduced and employed (Mackay and Diamond, 1989; Diamond et al., 1992; Hertwich et al., 2000). However, there are other features that make heavy metals troublesome to model. First of all, they speciate which means that they exist in different chemical forms some of which may precipitate (e.g., as sulphides in sediments) and which can also be transformed back. Also, their solid-water partitioning behaviour is highly influenced by the pH, the competing ions as well as available reaction partners present in the medium considered (e.g., Anonymous, 1999b). As many of them form cations they do not only bind to the (dissociated functional groups of) organic matter for example of soils but also to clays as well as to iron and manganese oxides/hydroxides (Jenne, 1998b). The latter have the unpleasant characteristic that they are not stable when redox conditions change.

However, as typical (i.e., Mackay-type) multimedia models are evaluative or screening models, they are fairly simple in that they divide the environment into rather large homogeneous boxes whose properties are constant over time (e.g., Mackay, 1991). Temporally variable conditions are usually not accounted for although attempts to allow for stochastic processes such as intermittent rain have been undertaken (e.g., Hertwich et al., 2000; Hertwich, 2001; MacLeod et al., 2001). Different from modelling degradation products of organic compounds where usually only the concentration of the parent compound and the respective reaction half-life are needed (see Fenner et al. (2000) for a discussion and a possible way out of this situation), modelling speciation of metals including adsorption involves knowledge about the ionic strength, pH and redox conditions as well as reaction kinetics and concentrations of the potential ligands or (highly heterogeneous environmental) adsorbents which can react with the heavy metals in the different media (e.g., Hering and Morel, 1990; Morel and Hering, 1993; Tompson, 1993; Turner, 1995; Ritchie and Sposito, 1995; Zachara and Westall, 1999).

Speciation is not included in the assessment at present due to two reasons: (a) the information on the different parameters influencing speciation is not existing at the geographical scope and for the spatial resolution employed; additionally the data on the physical-chemical properties of all species will most likely not be available either (Mackay et al., 1996b) and (b) setting up a multi-regional multi-media multi-species model (cf. United States - Environmental Protection Agency, 1999b) becomes too complex in terms of computation and data storage resources. A multi-species model may be considered in the future most likely on the expense of spatial detail. However, as pH can be considered one of the single most important parameters to influence the solid-water partitioning behaviour of heavy metals (cf. Sauvé et al., 2000), its dependence on pH is implemented in WATSON, the model whose development is described in this work. USES-LCA already included different compartment pH values although only for consideration of the behaviour of dissociating organic compounds (Huijbregts et al., 2000b).

3.2.4 Selected substances

Thus, mainly three criteria suggest to focus on the non-volatile heavy metals cadmium, lead and chromium as well as arsenic in the present study:

1. mercury and POPs such as PCDD/Fs, PCBs and benzo(a)pyrene require the modelling at the hemispheric or even global level (United States - Environ-

mental Protection Agency, 1997b; Ryaboshapko et al., 1998; Pekar et al., 1999) in order to cover the full impact pathway, especially in space; this is a main requirement when following the Impact Pathway Approach (cf. introduction to section 2.3) noting that lower bound estimates might also be informative,
2. heavy metals have until now only been poorly represented in multimedia models, and
3. the limited non-threshold effect information for ingestion (cf. Crettaz, 2000; Searl, 2002) suggests to further reduce the amount of trace elements addressed.

As a result, the rest of this work will focus on these trace elements. At times, also approaches for organic compounds will be provided for comparison and possible future methodological development reasons.

3.3 Need for development

None of the models presented in section 3.1 can be used for the calculation of external costs directly. Apart from the final external cost calculation (cf. Fig. 2-1), most of the models neither have the spatial coverage and resolution required, i.e., a rather detailed representation of Europe, nor provide exposure and/or impact assessment capabilities. If they allow for the assessment of effects these are mostly relying on Risk Characterisation Ratios (RCRs) that do neither take the magnitude of the effects nor their severity into account. They basically indicate whether there is concern or not. Additionally, the tools used in regulatory risk assessments usually introduce a fair amount of conservatism which does not allow the assessment of representative estimates.

However, there is one main exception as regards environmental fate and impact assessment in Europe which has been developed only recently: IMPACT 2002 (Pennington et al., 2005; cf. section 3.1.2). Nevertheless, shortcomings with respect to the purpose of the present study are:

- it does not cover the same area as the multi-source EcoSense version for Europe (Fig. B-1). As a result, some member countries (e.g., the Baltic states, Greece, Finland) of the European Union are not included. For the purpose of the present study, another reason for covering the same area as the existing EcoSense Europe versions is to provide estimates of the external costs that are comparable particularly to those for inhalation exposures assessed by these tools,
- the spatial resolution of both the environmental fate and exposure/impact model is rather coarse allowing for little spatial differentiation below the catchment level and only providing receptor data at the country level (e.g., human population, food production),

- it was developed for Life Cycle Impact Assessment (LCIA) purposes and does not cover the monetary valuation step necessary for cost-benefit analyses, and
- heavy metals and trace elements are covered only as a first attempt. A refinement is, therefore, deemed necessary. From the development of the metal-specific Dynabox model, it may be learned that the distinction of further compartments does not seem to influence the overall risk assessment from metal exposures (Heijungs, 2000). However, differences in the predicted soil concentrations of about one order of magnitude may occur.

The description of the respective model development is provided in the following Chapters.