



2-FUN

*Full-chain and UNcertainty Approaches for Assessing Health Risks in
FUture ENvironmental Scenarios*

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**– REVIEW OF FEATURES, EVENTS AND
PROCESSES INCORPORATED IN EXISTING MULTI-
MEDIA MODELS FOR FRESHWATER –**

**PROPOSAL OF THE CONCEPTUAL AND MATHEMATICAL
2-FUN MODEL FOR ASSESSING TRANSFER OF
CONTAMINANTS IN FRESHWATER**

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INTRODUCTION

The main objective of 2-FUN's WP2 is to build a software based on multimedia models and associated databases for assessing the exposure to chemicals through indirect routes (e.g. through the food chain). The specifications of this final product can be summarized as follows:

- to date, the simultaneous and comparative exposure assessment of various chemicals is difficult because: (i) models are generally dedicated to one specific family of contaminants (e.g. metals, or pesticides) or one type of emission/environmental media (e.g. soil); (ii) the representation of the macro- and micro-environments governing behaviour of chemicals in the environment and subsequent human exposure is not homogeneous among models; (iii) the level of mathematical simplification/sophistication and the mathematical description of common processes (e.g. physical processes which are independent of the stressor) can differ a lot among models. To overcome these limitations, the 2-FUN tool intends to allow a **homogeneous assessment of various chemicals, released in various systems and reaching humans through various routes**.
- environmental conditions differ in space and time, with temperature and region and so forth. Human behaviour differs with group, region, age, gender and so forth. Besides, there is real uncertainty, based on ignorance ("no-know") of processes or events. In exposure and risk assessment, this uncertainty is only indirectly considered by constructing typical ("generic"), conservative or "worst-case" scenarios. This may give estimates "on the safe side", but does not allow a quantification of this safety. However, environmental variations (space, time, temperature, region) can in many cases be quantified and described, e.g. by probability density functions on key parameters. The same holds for differences in human behaviour. The objective of the 2-FUN tool is then to incorporate **distributed input data for the exposure assessment** (stored in an ad-hoc database), yielding a **distributed output**. The 2-FUN tool would then allow the quantification of the probability of an individual to be exposed, allowing a safety concept that substitutes the 'conservative' concept.
- To date, research on the **exposure profiles of children** to identify the most important routes of exposure are scarce. To incorporate specific children's pathways in exposure models, a review of the existing literature on children's exposure routes (e.g. epidemiological studies aiming at identifying exposure routes of organics, lead or radionuclides) will be conducted and relevant pathways (e.g. physiological parameters, behavioural parameters and time-activity data for different age groups) will be introduced into the multi-media model(s).

This report is the first stage to the construction of the 2-FUN's homogeneous and integrated software for the assessment of indirect exposures. Features, Events and Processes (FEPs) occurring within and/or between environmental compartments of interest for humans were reviewed considering existing models/frameworks/methodologies currently used for conducting human risk assessments. This report is specific to FEPs occurring in freshwaters¹.

A systematic method for the visualization of FEPs contained in each model (i.e. the Interaction matrix method) was used to compare models. The relevance of each FEP for its eventual incorporation into the 2-FUN model was studied. Finally, a list of relevant compartments and associated FEPs to be included into the 2-FUN modelling system will be proposed.

The mathematical model for describing the transfer of contaminants to/within/from freshwaters is also described in detail.

¹ Further reports will be published on other sub-systems of the environment (soil and groundwater, outdoor atmosphere and indoor air, plants, animals, humans)



1. MATERIAL AND METHODS

1.1 Perimeter of the 2-FUN modelling tool

The 2-FUN modelling tool will focus on the detailed description of the transfer of chemicals through the human food chain. Thus, the 2-FUN modelling tool considers a region of investigation (a 'box') for which inputs at its frontiers are known. In other words, the 2-FUN model will use as input data:

- monitoring data directly collected at the frontier of the investigated region in surface water, air and/or soils;
- data produced by models simulating the physical transport (e.g. advection/diffusion/dispersion) of pollutants in the air or in water bodies from the release point(s) to the frontier of the investigated region, and providing concentrations of pollutants in air, soil and/or water entering in the investigated region.

According to available data related to the contamination in water, air and/or soil at the assessment point, the 2-FUN modelling tool will consider:

- steady-state conditions, when permanent discharges into the environment are assumed;
- dynamic conditions, if time-dependent data are available (e.g. incidental/accidental discharges).

1.2 Sub-systems of the environment

The first step in the development of a biosphere model is the construction of a conceptual model defining the biosphere system components, e.g. air, water, soil, crops, animals etc, eventually subdivided in several sub-compartments, as well as the relations between these components (i.e. transfers governed by physical, chemical and/or biological processes). Thus, compartments taken into account into multimedia models are the media in which chemicals may migrate or accumulate.

For facilitating the analysis of existing models and proposing an integrated framework for the further development of the 2-FUN modelling tool, six main sub-systems were defined:

- the 'surface freshwater' system;
- the 'soil' and 'groundwater' system;
- the 'air' system, including outdoor atmosphere and indoor air;
- the 'plant' system;
- the 'animal' system;
- the 'human activity' system.

The present report focuses on the surface freshwater subsystem. The other subsystems will be reviewed in the second period of the 2-FUN project.

Besides, a specific analysis and associated report will be produced for specific exposure pathways for children (Deliverable 2.2: review of relevant exposure pathways for children).

1.3 Mass-balance concepts

The 2-FUN model was built to maintain a mass balance in the whole system, as well as in each of the sub-system previously defined. When applied to a specific compartment, the mass balance approach implies that, for a given time period, the amount of chemical in the compartment at the end of the periods results from the amount present at the beginning plus the gains occurring during the time period minus the chemical lost from the compartment.

The geometry of the investigated region is assumed to be known by the end-user, i.e. the length, width and height of the river/lake system, the surface of the soil system, as well the distribution of occupancy of the soil system by different cultures (including forest), ...



1.4 The Interaction Matrix methodology

Interaction matrices, an expert qualitative method to identify multiple interactions among biotic and abiotic components of the biosphere, is a useful tool to develop conceptual models simulating the behaviour of chemicals in a complex environment. This systematic approach facilitates a comprehensible identification and visualization of the exposure pathways and allows classification of the role of different ecosystem components in terms of transfer relationships.

An Interaction Matrix is a table which describes the conceptual model by tabulating the interactions between the compartmental media. The main compartments of the biosphere system are identified and listed in the leading diagonal elements (LDEs) of the matrix; the interactions between the LDEs are listed in the off-diagonal elements (ODEs) (Figure 1).

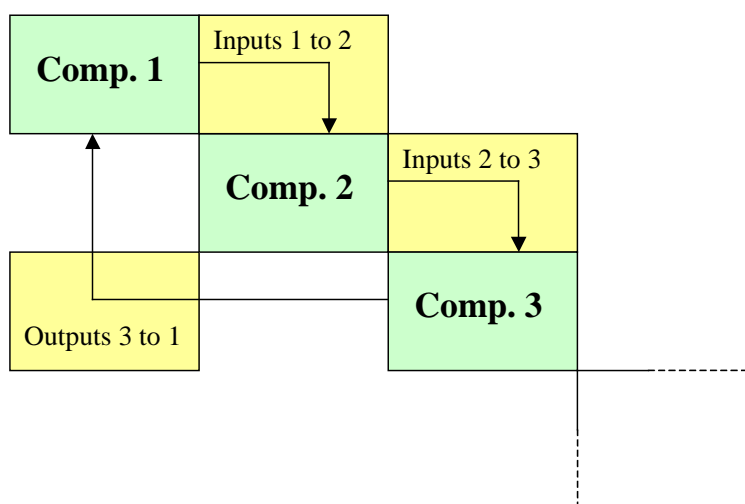


Figure 1 – The Interaction Matrix presentation

The Interaction Matrix will support the further mathematical implementation of the conceptual model²: the LDEs will usually be represented by compartments and the ODEs by transfer functions. Using the matrix as a complete representation of the conceptual model, it is relatively simple to cross-check it against a standard Features, Events and Processes (FEPs) list to ensure that the conceptual model is as complete as a specific context requires.

Obviously, there may be different alternative mathematical models for each FEP, as well as several numerical models for each mathematical model. Mathematical models describing the Interaction matrices reviewed in the present document will not be detailed here. Only the final 2-FUN mathematical model is described in detail in chapter 4.

² the implementation will be conducted on the Ecolego® platform, specifically built for compartmental models described through an Interaction Matrix.



1.5 List of reviewed models

For defining the 2-FUN conceptual model, existing models/frameworks/methodologies currently used for conducting risk assessments in specific fields (e.g. risk assessment of contaminated soils) were reviewed; a given model/framework/methodology covers all the sub-systems defined in 1.2 (i.e. the ‘surface water’ system, the ‘soil’ and groundwater system, etc) or only some of them. Material which was reviewed is listed in Table 1.

Two types of models/frameworks/methodologies were reviewed:

- Integrated multimedia models, covering all the water, soil, and biota sub-systems and aiming at calculating global human exposures (e.g. SimpleBox, CalTox);
- Fate models, providing a detailed description of the behaviour of chemicals in a specific sub-system (e.g. AQUATOX for the freshwater subsystem).

The list of models which were reviewed is not exhaustive, but we selected some contrasting tools (e.g. from screening models to detailed mechanistic ecological models) in order to underline possible divergences in the treatment of pollutant transfer in a given sub-system. The analysis of the models thus allowed to put in evidence some main questions when building a conceptual and mathematical multimedia model.

Table 1 – List of reviewed models/frameworks/methodologies for the freshwater system

Model	Description	Institute	References
AQUATOX	Ecological food-web freshwater model kinetically describing transfer of chemicals in various abiotic and biotic compartments. Dynamics of several trophic levels in aquatic systems (streams, small rivers, ponds, lakes and reservoirs), as well as the fate of conventional (e.g. nutrients) and toxic chemicals are simulated. This food-web model was developed for evaluating the adverse effects from various stressors on several trophic levels (the endpoint is thus not human health).	US-EPA	US-EPA, 2004
CemoS (similar to SAMS (OECD))	Mass balance steady-state box model included in the CemoS package	DTU (Dk)	Trapp and Matthies, 1998
OURSON	Dynamic transfer initially developed for simulating the human exposure to radionuclides and metals discharged in freshwater. Extended to metal discharges in the atmosphere and organic discharges in rivers	EDF (F)	Ciffroy, 2006 ; personal communications
QWASI (and derived models QMX, DynA)	Model simulating the steady-state chemical concentration in a lake or river segment. It adopts a steady-state fugacity approach, each transfer being described by constant exchange rates. QMX is an extension of QWASI using a connectivity matrix to develop a multi-segment approach.		Mackay, 1983; Di Guardo, 2006; Warren et al, 2007
SimpleBox	Steady-state multimedia model incorporated in the EUSES system, recognized at European for assessing the distribution of (essentially organic) pollutants in the environment at regional scale.	RIVM (NL)	Van de Meent, 1993; Brandes, 1996
TRIMFate	Compartmental mass balance model providing exposure estimates for ecological receptors (plants and animals), in particular in freshwater systems. The output concentrations from TRIM.FaTE can also be used as inputs to a human ingestion model.	US-EPA	US-EPA, 2002

1.6 Selection of relevant FEPs for the 2-FUN conceptual model

One main question when building a conceptual multimedia model is to define its optimal size, i.e. to define which are the compartments and FEPs sufficiently relevant for their incorporation into the model. Indeed, the most exhaustive conceptual model, i.e. those which contains the most important number of compartments and FEPs is not necessary the most relevant for operational applications in a wide range of contexts. Indeed, the objective should be, not to build the most complete model, but

rather the less uncertain one. Taking in mind this objective related to uncertainty (rather than to exhaustivity), a conceptual model must thus be the result of a compromise between a relevant representation of the environment and the uncertainty of data to make the model an operational tool.

This concept is illustrated on Figure 2. When the conceptual model becomes more complex, i.e. when the environment is described more in detail, with an increasing number of compartments and FEPs, the structural uncertainty of this conceptual model decreases, because it can be considered that the structural representation is closer to the actual environment.

Parameter uncertainty should however be taken into account also. It can be subdivided in different components which depend on the structure of the model: natural variability, reflecting the heterogeneity in a given compartment; incompleteness, reflecting the 'macroscopic' nature of the environment description by the model; and ignorance, reflecting the lack of knowledge and/or data for a relevant parameterisation of a given transfer. If the model is too simple (i.e. if the representation of the environment is based on macroscopic compartments and/or transfer functions), the structural uncertainty, but also the variability and incompleteness of parameters, are high. However, when the conceptual model becomes too complex, the number of parameters and data required for running the modelling system, and the associated ignorance, increases; often a complex conceptual model requires data which are scarcely available and is based on unknown processes, leading to the increasing of the parametric uncertainty.

This schematic representation shows that the challenge for modellers is to build the less uncertain model, i.e. the best compromise between conceptual environmental representation and knowledge/data availability.

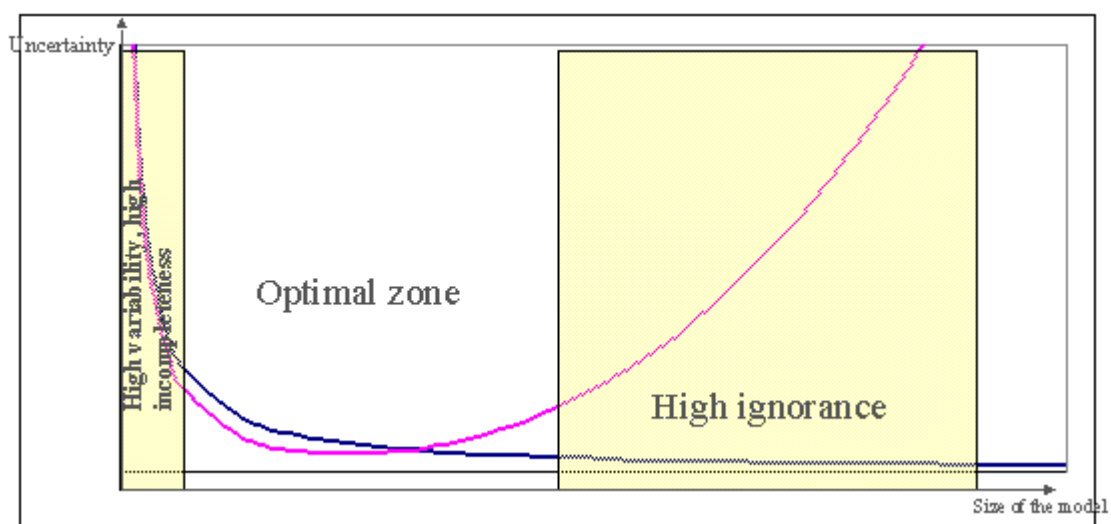


Figure 2 – Evolution of the uncertainty of the conceptual model and of data according to the complexity of the environment representation

The review undertaken in the frame of the 2-FUN project allowed to identify different conceptual models, with variable levels of complexity. An analysis of models was thus conducted, from the simplest one to the most exhaustive one, with in parallel an analysis of new information required when adding compartments and FEPs, and expert judgement described in the report allowed to define the best compromise to build the 2-FUN model. The objective of this analysis is to build a conceptual model in agreement with data availability that will be further incorporated in the tool database.

2. THE SURFACE FRESHWATER SYSTEM – REVIEW OF MODELS

2.1 Interaction matrix of investigated models

Models which were analysed for the surface freshwater system are listed in §1.5. Their respective Interaction matrices are represented in Figures 3-7³.

Upstream Water flow			Upstream input	Upstream input				
	Atmosphere	Direct atmospheric deposition	Direct atmospheric deposition	Direct atmospheric deposition				
		Soil surface	Erosion-runoff	Erosion-runoff				
			River/lake water Dissolved phase	Adsorption			Bioaccumulation	
			Desorption	River/lake water Suspended particulate Matter	Particles deposition			
				Particles resuspension	Bottom sediments			
						Fish		Biological elimination
								Sink

Figure 3 – The OURSON Interaction Matrix for the surface freshwater sub-system

Upstream Water flow				Upstream input					
	Atmosphere Gas phase			Gas absorption					
		Atmosphere Aerosols		Wet and dry deposition					
			Soil	Runoff					
	Volatilization			River/lake water Dissolved phase	Adsorption	Uptake by adsorption		Bioaccumulation	Outflow Transformation
				Desorption	River/lake water Suspended particulate Matter	Sedimentation			
				Release by desorption	Resuspension	Bottom sediments Top layer	Burial		
							Bottom sediments Deep layer (sink)		
				Elimination				Biota	
									Sink

Figure 4 – The SimpleBox Interaction Matrix for the surface freshwater sub-system

³ In the following Interaction matrices, compartments are represented in green, transfers between compartments in yellow and 'sink' compartments in pink.

Upstream Water flow		Upstream input	Upstream input			
	Atmosphere	Dry and wet particle deposition Rain dissolution Absorption				
	Volatilization	River/lake water Dissolved phase	Adsorption	Diffusion		Downstream water flow Transformation
		Desorption	River/lake water Suspended particulate Matter	Particles deposition		Downstream water flow
		Diffusion	Particles resuspension	Surface sediments	Diffusion	Transformation
					Buried sediments	
						Sink

Figure 5 - The QWASI Interaction Matrix for the surface freshwater sub-system

Waste water flow		Dilution - Advective transport Elimination from the release point				
	Atmosphere Gas phase	Gas absorption				
	Volatilization	River/lake water Neutral dissolved phase	Adsorption		Bioaccumulation	Aggregated degradation
		Desorption	River/lake water Suspended particulate Matter	Sedimentation		
			Resuspension	Bottom sediments		
		Elimination			Fish	
						Sink

Figure 6 - The CemoS Interaction Matrix for the surface freshwater sub-system

Figure 8 – The TRIM.FaTE Interaction Matrix for the surface freshwater sub-system

2.2 The compartments of the freshwater system

The freshwater system can be analysed considering three main sub-systems: the water column, the sediments and the biota:

- for all the models (except AQUATOX), the water column is sub-divided in two compartments: the contaminant fraction present under dissolved forms, and the contaminant fraction associated to suspended particles. It may be noted that, for the CemoS model, it is indicated explicitly that this subdivision is relevant only for neutral organics, and not for dissociated organics.

AQUATOX proposes a more sophisticated representation of the water column: for lake and reservoir applications, it subdivides the aquatic system into two vertical zones, respectively the epilimnion and the hypolimnion. The thermocline is taken as separator and, for simplicity, it is assumed to occur at a constant depth. Stratification can break down temporarily in case of high flow. The particles present in suspension in raw water are subdivided in several compartments, including: inorganic particles, labile detritus and refractory detritus. Detritus include all non-living organic material. The definition of detritus compartments was considered necessary to provide a good description of the detrital food web. Buried detritus are also defined as not participating to the exchanges;

Question 2.a: how many abiotic compartments for representing the water column ?

- models differ in their representation of the sediment compartment because:
 - ✓ for OURSON, only one layer is considered for describing sediments present at the bottom of the river or lake bed;
 - ✓ two layers are considered in the other models for representing bottom sediments: the top layer of the sediment is in interaction with the water column; if the sedimentation of particles from the water column is greater than the resuspension (net sedimentation), the top layer is continuously refreshed and chemicals associated to older sediment layer gets buried under the top layer ('buried sediments'). In most of these models (e.g. the SimpleBox model), the terminology 'sediment' refers only to the top layer, as the deeper sediment is assimilated to a 'sink' compartment which does not participate to the exchanges. This approach needs to define the frontier between surface sediment and deep sediment respectively, i.e. the depth at which sediments can be considered as 'out' of the system.

Question 2.b: how many layers for representing the sediments?

Question 2.c: is it necessary to take into account 'burial' and how to define the frontier between top layer and deep sediment?

- the representation of biota differs according to the objectives of the model:
 - ✓ because AQUATOX and TRIMFaTE were developed for assessing acute and chronic effects on biota (to various aquatic species in this specific context), many biological compartments, corresponding to several trophic levels, were defined in the model (e.g. algae, macrophytes, invertebrates and fish for AQUATOX; algae, macrophytes, benthic fauna and several fish groups for TRIMFaTE) and can lead to biomagnification processes. The modelling system is based on a food-web analysis, the contamination rate of one biological compartment depending on its direct bioaccumulation from water (sediment pore water for benthic organisms in TRIMFaTE), but also on its diet (consumption of contaminated food).
 - ✓ OURSON, SimpleBox and CemoS consider only one single 'fish' or 'biota' compartment (according to the terminology used in OURSON/CemoS and SimpleBox respectively⁴), assumed to be uniform and of interest for human diet.

⁴ For SimpleBox, a global biological component called 'biota' is included in the model, referring to all living organisms in water, and especially to fish. Thus, 'Biota' constitutes a generic compartment without any distinction of species, age, etc.

Question 2.d: how many species for representing biological compartments of interest for humans?

Question 2.e: is it necessary to develop a food-web model to simulate the transfer to fish?

2.3 The inputs/outputs into/from the freshwater system

Several main sources of contamination of the freshwater system at the investigated site can be considered:

- chemicals entering into the system from upstream inputs of contaminated water are considered in all the models (except AQUATOX, the initial concentration of toxicants in the aquatic system being assumed to be known, and, as a consequence, the inputs into the system being not explicitly defined). For the OURSON model, it is specified that, if discharges are at a long distance from the investigated region, or in case of diffuse inputs along the river watershed, the (steady-state or time-dependent) upstream contamination level requires the use of other advection/diffusion/dispersion models. The CemoS model considers an average dilution factor and transport time from the release point to the investigated region for calculating the total concentration entering into the box. For SimpleBox, input of contaminated water across the system boundary can be considered at different scales, i.e. across the continental, regional or moderate scale;
- direct dry and wet deposition of contaminants present in the atmosphere are considered in all the models (except AQUATOX and CemoS). Dry deposition is generally simulated through a constant deposition velocity of the aerosols particles, while wet deposition (or washout) is related to rainfall by a scavenging ratio (i.e. the ratio between the contamination in rainwater and in air respectively);
- some models (SimpleBox, QWASI, TRIM.FaTE, CemoS) also consider transfer of atmospheric gaseous pollutants to river water, but approaches for simulating it differ:
 - ✓ absorption of gaseous contaminants present in the atmosphere, and inversely, volatilization of dissolved contaminants to atmospheric gas are considered in SimpleBox and QWASI. The overall mass transfer coefficient for gas absorption is estimated by a two-film resistance model at the air-water interface, resulting from the summation of resistances at the air and water sides respectively. The volatilization mass transfer coefficient is calibrated by taking into account mass transfer for gas absorption, in order to maintain a permanent equilibrium at the water-air interface. In AQUATOX, volatilization is modelled using a two-film model, diffusion rates of chemicals being related to known diffusion rates observed for oxygen or water vapour.
 - ✓ for TRIM.FaTE, an advective flux of vapour-phase chemicals is calculated, but as the result of wet deposition: as rain falls, it is assumed to gather vapour-phase chemicals from the air, coming into equilibrium with the fugacity of the air compartment. The QWASI model also considers the input of contaminants dissolved in the rain; it is thus distinguished wet deposition of aerosols, and rain dissolution;

Question 2.f: is it necessary to include both 'diffusion' and 'rain dissolution' processes in the exchange of vapour-phase contaminants at the atmosphere-freshwater interface ?

- in OURSON, SimpleBox and TRIM.FaTE, indirect inputs from atmospheric contamination through the pathway 'Atmosphere → Direct deposition on soils → erosion and/or runoff are considered. However, the approach for modelling this pathway highly differ:
 - ✓ in OURSON, the input is simulated by a time-dependent transfer function taking into account the deposition fluxes from the atmosphere to the soil and the delay separating the atmospheric deposition and the assessment date (assuming that transfers decreases exponentially over time);

- ✓ in SimpleBox, 'Soil to water' transfer by runoff and erosion are taken into account, considering the (constant) fraction of rain water running off from soil to water, and a rate at which soil particles are washed to surface water;
- ✓ in TRIM.FaTE, runoff is modelled as a continuous process (although it is assumed to occur only during rain events), assuming an equilibrium between rainwater and pore water of the surface soil. This model requires the use of several parameters, such as the average 'fraction of water running off of surface soil, the 'fraction of surface soil available for runoff'. It is indicated that these parameters must previously be estimated by site-specific characteristics (e.g. slope of the flow). The modelling of erosion is similar to those developed for runoff, but it concerns soil solids instead of pore water.

Question 2.g: which are the best assumptions to include runoff/erosion processes (direct relationship with atmospheric deposition, constant rain water reaching surface water, mechanistic model requiring site-specific geographical characteristics ?

- transformation processes in raw river water and sediments are considered in all the models for organics. Degradation processes are generally simulated by pseudo first order degradation rates (i.e. degradation proportional to the concentration of contaminants in the media). However, transformation processes are described in detail in AQUATOX, which explicitly distinguishes the following processes: (i) hydrolysis (acid- and base-catalyzed hydrolysis are modelled according a thermodynamic principle); (ii) photolysis (calculated for the epilimnic zone, taking into account light intensity); (iii) microbial degradation (calculated by a maximum microbial degradation rate, eventually attenuated by anaerobic conditions, suboptimal temperature and suboptimal pH). In other models, biodegradation, photolysis and volatilization are separated, but added into an aggregated loss rate.

Question 2.h: is it sufficient to use a 'global' degradation rate implicitly including several degradation processes?

2.4 The inter-compartment transfers within the freshwater system

Several transfer are considered between components belonging to the freshwater system:

- exchanges of contaminants between the dissolved and the particulate phases of the water column. In all the models (except AQUATOX), these exchanges are assumed to be equilibrated, and thus described by a distribution (or partition) coefficient, expressed as the concentration ratio between the particulate phase and the dissolved phase respectively. For organic pollutants, exchanges are governed by a hydrophobic sorption mechanism and the distribution coefficient is related to the octanol-water partition coefficient and the concentration of organic matter in the particles. In AQUATOX, exchanges between water and detritus or inorganic particles are described by non equilibrium kinetics, using sorption and desorption kinetic rate constants;
- exchanges of particulate contaminants between the water column and bottom sediments. Two types of processes are potentially included in the models: (i) deposition and resuspension of particles (and of associated chemicals linked to them) at the water column-bottom sediments interface, and (ii) chemical exchanges of contaminants between the sediments and the water column by diffusion. For the first process, two different approaches were considered
 - ✓ in SimpleBox, QWASI and TRIM.FaTE, sedimentation and resuspension of particles are simulated considering constant sedimentation and resuspension rates (expressed of downstream and upstream velocities of particles, in $\text{m}\cdot\text{s}^{-1}$), occurring simultaneously. In case of net sedimentation (i.e. deposition > resuspension), this approach would lead to an 'infinite' accumulation of particles in the bottom. This effect is compensated by the incorporation of a 'burial' process, acting as a transfer to

a sink compartment. For example, in SimpleBox, the burial rate (i.e. the mass flow from the top layer to the deeper sediment) is assumed to be equal to the net sedimentation rate (i.e. deposition minus resuspension), and thus the top layer of the sediment is continuously refreshed and its depth is maintained constant

- ✓ in OURSON, deposition and resuspension can not occur simultaneously and depend on the hydraulic and morphological characteristics of the river or lake: deposition occurs when water velocity is low enough and thus when the shear stress is lower than the critical deposition shear stress, while resuspension occurs only if water velocity exceeds a given critical value (e.g. during flood events). As dynamics of sediments are simulated (and refreshment of sediments potentially occurring during floods), no burial is assumed.

Question 2.i: what is the good approach to simulate particulate physical exchanges at the water-sediments interface: equilibrium model requiring burial, or dynamic model requiring hydraulic data ?

In all the models (except OURSON), chemical exchanges of contaminants between the sediments (top layer) and the water column are considered. An overall mass transfer coefficient for direct adsorption/desorption across the sediment-water interface is defined, assuming that the exchanges are governed by a two-film resistance model. This model requires values regarding diffusivities for the water and pore water sides, as well as for describing the diffusion length. In OURSON for metals, chemical exchanges by diffusion at the water/sediment interface are not considered in the model because it is considered that physical processes previously described are predominant.

Question 2.j: is diffusion a predominant process compared to deposition/resuspension for water-soluble compounds ?

- The transfer of contaminants to biota (one or several sub-compartments according to the models - see 2.2) is simulated according to two different approaches:
 - ✓ in SimpleBox, equilibrium is assumed at all times among water and biota, through an equilibrium Bioconcentration Factor.
 - ✓ in the OURSON model, the uptake of contaminants by fish is simulated by a Bioconcentration Factor, expressed as the concentration ratio between the fish concentration and the dissolved concentration in freshwater (and not the raw contamination) at equilibrium. However, dynamic process was introduced by a biological elimination rate, leading to a first order kinetics in the concentration of contamination in fish. Contaminant eliminated from fish is assumed to be transferred to a 'loss' compartment, and not recycled to freshwater, because it is supposed that the pathway river water → accumulation into fish → release to raw freshwater does not significantly influence the mass budget in raw river/lake water. To avoid numerical complications, the recycling is then neglected.
 - ✓ in AQUATOX, transfer of toxicants from water to biota (algae, macrophytes, invertebrates and fish gill) is kinetically simulated, taking into account bioconcentration factors, but also first order clearance rates. For fish, not only transfer from water is taken into consideration, but also dietary uptake. This pathway was incorporated into the model to take into account potential biomagnification processes. The ingestion of contaminated prey by fish (gut system) is thus simulated, associated with an efficiency of sorption by gut.
 - ✓ For fish, TRIM.FaTE proposes a Bioenergetic-based kinetic model, assuming direct uptake from water but also indirect uptake by diet.

Question 2.k: is it sufficient to consider an equilibrium bioconcentration factor or is it necessary to incorporate also kinetic elimination/clearance rates ?

Question 2.1: **is it sufficient to consider direct transfer from water or is it necessary to include food intake routes ?**

3. THE SURFACE FRESHWATER SYSTEM - DEFINITION OF THE 2-FUN INTERACTION MATRIX

The comparison between several multimedia models allowed to put in evidence some important questions which must be discussed for the definition of the 2-FUN Interaction Matrix. These main questions will be reviewed in this section.

3.1 Compartments of the water column

This section intends to provide elements for answering to the question 2.a: **how many abiotic compartments for representing the water column ?**

Distinguishing substances under their dissolved forms and suspended particulate forms respectively is a minimum requirement for multimedia models because of the different subsequent behaviour of pollutants according to their speciation: dissolved pollutants are more easily available for biota than particulate forms; on the contrary, particles can be accumulated in sedimentation zones and constitute potential secondary source of contamination (especially during floods). The 2-FUN model will consequently distinguish dissolved contaminants and contaminants associated to suspended particles.

A more detailed description of the water column (as those available in the AQUATOX model, where inorganic particles and organic detritus are distinguished and where two vertical zones (epilimnion and hypolimnion respectively) are considered for lakes) is however out of the scope of the 2-FUN model because of the scarcity of data for the parameterisation of such models: the distinction between inorganic and organic particles would require distribution coefficients for these two phases, while most of distribution coefficients experimentally determined in the field or in laboratory are derived for the natural particulate phase globally. Besides, a spatial description of lakes would be relevant only if associated data are available, such as temporal dynamics of stratification/destratification, movement of biota across the two zones governing its contamination, etc. Such data being scarcely available for human risk assessments, the freshwater system will be considered as a homogeneous system without vertical stratification.

3.2 Processes involving the sediment compartment

3.2.1 Description of the sediment/water interactions: steady-state vs dynamic models for describing deposition and resuspension of particles

This section intends to provide elements for simultaneously answering to the questions 2.b, 2.c and 2.i:

How many layers for representing the sediments?

Is it necessary to take into account 'burial' and how to define the frontier between top layer and deep sediment?

What is the good approach to simulate particulate physical exchanges at the water-sediments interface: equilibrium model requiring burial, or dynamic model requiring hydraulic data ?

Many models include deposition and resuspension of particles as a potential exchange pathway at the suspended matter-sediment interface. However, behind this consensus regarding the importance of this pathway, two main mathematical approaches, summarised in the following table, are proposed in the reviewed models.

Table 2 – Limits and advantages of steady-state and dynamic approaches to represent physical exchanges at the water-sediment interface

Approach	Assumptions and data requirement	Limits	Advantages
Steady-state model	Deposition and resuspension of particles occur simultaneously	Non realistic assumption for many rivers submitted to seasonal variations in the flow rate leading to temporal cycles of deposition/resuspension (floods)	
	Constant deposition and resuspension rates (e.g. kg suspended particles.m ⁻² .d ⁻¹ for deposition and in kg benthic particles.m ⁻² benthic sediment.d ⁻¹ for resuspension) are required	The calibration of the parameters should be site-specific and should require data on hydraulics of the system.	Only two parameters are required
	To compensate the continuous accumulation of sediments resulting from a constant positive net deposition, models generally include a burial process, old sediments being considered as inactive and assimilated to a sink compartment	The model is highly dependent of the choice of the active sediment depth (surface layer)? Or, how to define the burial rate?	
Mechanistic dynamic model	Deposition and resuspension do not occur simultaneously and are governed by the time-dependent hydraulic conditions (deposition occurring at low water velocity and resuspension at high water velocity (e.g. during flood periods))		Realistic for river conditions
	Data related to hydraulic conditions of the freshwater system (i.e. time-dependent velocity, or flow rate and main geometric characteristics of the system allowing the calculation of water velocity) are required	Site-specific and temporal data regarding hydraulics of the system must previously be collected	Flow rates and geometry of the river/lake are generally available
	Physical parameters are required (e.g. settling velocity of particles, critical velocities for deposition/resuspension, erosion rate)		These parameters have a physical meaning. Orders of magnitude are available in the literature

Briefly, the use of steady-state conditions appears not to be realistic for many aquatic systems. Steady-state assumptions lead indeed to a permanent accumulation of particulate material in bottom sediments, without any release. This effect is compensated by the introduction of a burial process which can be assimilated to a transfer to a sink compartment. Thus, it appeared that the simplicity of the approach needs to be compensated by the addition of an other process not easily parameterised (i.e. how to define the ‘burial’ rate?). A mechanistic dynamic model based on physical assumptions developed in sedimentology appears to be more realistic. Besides, even if more parameters and data (e.g. time-dependent flow rates and mean geometry of the aquatic system) are required, these latter are generally available for rivers and lakes.

In conclusion, it can be recommended to introduce a dynamic description for physical exchanges at the suspended matter-sediment interface. Dynamic description will also allow to use the model under short term conditions (e.g. accidental conditions), where deposition or resuspension do not necessarily occur.

3.2.2 Description of the sediment/water interactions: role of diffusion

This section intends to provide elements for answering to the questions 2.j: **is diffusion a predominant process compared to deposition/resuspension for water-soluble compounds ?**

Most of the models consider two main pathways for describing the exchanges of chemicals at the ‘water column-sediment’ interface:

- exchanges governed by physical processes, i.e. deposition and resuspension of particles;

- exchanges governed by chemical exchanges, i.e. diffusion of chemicals at the ‘pore water-surface water’ interface, the direction of exchanges being determined by the chemical gradient between these two compartments.

As two processes participate in parallel to the exchanges between the water column and the sediment, it is justified to wonder when the transfer due to one given process (e.g. diffusion) will dominate the total substance mass transfer, and thus to know whether the two processes actually need to be represented.

Sørensen et al (2001) conducted a critical analysis of the generic compartmental description used (for example, in the SimpleBox model) to represent the diffusion process at the water-sediment interface. In particular, the relative contributions of physical (i.e. particles deposition) and diffusive processes respectively were assessed. The conclusions of their study are:

- under transient conditions, diffusion is an important exchange pathway only during a limited time scale, just after the start of emission, because of large gradients at the sediment surface. However, as time progresses, the diffusion-induced flux rapidly decreases, as the concentration gradients at the top of the sediment decreases. In contrast, deposition-resuspension of particle-bound contaminant is not governed by gradients at the sediment-water interface and thus become predominant over long time scales. Sørensen et al (2001) propose a decision rule scheme to assess whether diffusion is a negligible process or not in comparison to physical exchange processes. This decision rule scheme is based on the calculation of a critical time period, in function of the molecular diffusion coefficient in sediment pore system, the retention factor for the sediment as a result of adsorption and the deposition settling velocity. From this scheme, it can be concluded that it is relevant to include diffusion in multimedia modelling only in some limited cases, e.g. for transient short term conditions (like accidental conditions);
- when diffusion is a predominant exchange pathway at the water-sediment interface, the description of diffusive transfer is not well established by the one-box model generally used in multimedia models (like SimpleBox), which underestimates mass transfer because of the assumption of mean transfer length.
- in current models, bioturbation is not taken into account (except in some models like CoZMo (Wania, 2006) not described in detail here) while it may induce a vertical mixing of water and sediment solids and thus enhance diffusive transfer.

It can be concluded from this study that physical transfer associated to deposition and resuspension of particles are generally the predominant pathways governing contaminant exchanges at the water-sediment interface. The generic compartment model classically proposed in multimedia models (such as SimpleBox and QWASI) for describing diffusive transfer can thus be seen as a screening method allowing to verify that this pathway does not play a significant role in the exchanges and that a more detailed model is not actually needed.

In conclusion, in the perspective of a wide application of the 2-FUN system (e.g. for short term pollutions occurring under accidental conditions), it is suggested to include the diffusive transfer at the water-sediment interface in the 2-FUN conceptual model. However, as this process is a priori not predominant in most of the situations, it is recommended to adopt (as screening method) the generic approach already included in existing multimedia models like SimpleBox or QWASI, rather than a more sophisticated representation. The importance of diffusive pathway on the transfer from and to sediments and thus as a secondary source of contamination will thus be checked.

[3.3 The air-freshwater interactions](#)

This section intends to provide elements for answering to the question 2.f.:
is it necessary to include both ‘diffusion’ and ‘rain dissolution’ processes in the exchange of vapour-phase contaminants at the atmosphere-freshwater interface ?

Two main processes are generally included in multimedia models for simulating the input of pollutants from atmosphere to freshwaters:

- dry deposition of pollutants associated to aerosols, generally simulated through a constant deposition velocity of the aerosols particles;
- wet deposition, i.e. deposition associated to precipitations, generally simulated by a scavenging ratio describing the entrainment of pollutants associated to aerosols during rain events.

These two processes regards the input of pollutants associated to aerosols in the atmosphere, but do not represent exchanges with vapour-phase contaminants. Some models consider also (often partially) the exchanges concerning these latter:

- dissolution of gaseous pollutants in rain and subsequent wet deposition. This process can be simulated in an analogous way as for aerosols, i.e. through the use of a scavenging ratio (Sportisse, 2006);
- absorption/volatilization of vapour phase pollutants is generally interpreted in analogy to electrical resistance, but several approaches are possible to simulate this process: (i) the deposition to the surface can be assumed to be controlled by three resistances in series (aerodynamic, quasi-laminar layer and surface resistances). A deposition velocity is thus computed from these three resistances and allows to calculate dry deposition of gaseous pollutants (Wesely, 2000); (ii) the fugacity approach assumes the presence of two resistances in series (stagnant water layer and stagnant air layer) governing both absorption and volatilization of gaseous pollutants. In the 2-FUN model, the latter approach was chosen because it offers the advantage of taking into account both deposition and volatilization of gaseous pollutants.

In conclusion, it appears useful and possible to parameterize five processes for simulating the input of pollutants from the atmosphere to freshwaters, i.e. dry and wet deposition of aerosols, gaseous wet deposition following rain dissolution, and absorption/volatilization at the atmosphere/water interface.

[3.4 The soil-freshwater interactions](#)

This section intends to provide elements for answering to the questions Question 2.g: **which are the best assumptions to include runoff/erosion processes (direct relationship with atmospheric deposition, constant rain water reaching surface water, mechanistic model requiring site-specific geographical characteristics) ?**

Pollutant wash-off (runoff of dissolved contaminants and erosion of contaminated soil particles) from watersheds can be a significant secondary input into freshwaters because these latter collect water and particle fluxes from potentially wide areas, especially during rainfall. The input of pollutants from watershed to freshwaters can be simulated by different approaches:

- a transfer function can be used to directly relate atmospheric depositions (or succession of depositions in case of chronic fluxes) in the watershed and the concentration in river water. This approach was especially used in radioecological models, the calibration of transfer functions being possible after the Chernobyl accident for a wide range of European rivers (single atmospheric pulse with well-known spatial mapping of soil contamination and follow-up of rivers contamination during short and long periods after the deposit) (Garcia-Sanchez et al, 2007);
- it may be assumed that a constant proportion of rain water reaches freshwater systems (as in SimpleBox) and that this fraction is in immediate equilibrium with soil (same concentration and same partition between water and particles described by the soil distribution coefficient).
- a mechanistic model (eventually coupled to a fugacity model, as in TRIM.FaTE) can be used to simulate storm-water runoff. Such models calculate a hydraulic balance in soil to determine the flow of runoff water and the depth of runoff stream. They thus require site-specific data.

The advantages and limits of these approaches are summarised in the following table.

Tableau 3 – Limits and advantages of steady-state and dynamic approaches to represent physical exchanges at the water-sediment interface

Approach	Assumptions and data requirement	Limits	Advantages
Transfer function	Transfer function empirically calibrated (essentially after the Chernobyl accident)	Calibration only for a limited set of substances	- Calibration for a wide set of European watersheds; - Calibration for short-term and long-term after deposition (possibility of kinetic model); - Inter-substances extrapolations are possible because transfer essentially depends on solid-liquid partition; - No need of additional meteorological data
Constant rainwater running off to rivers	Fraction of rainwater reaching freshwater systems	Highly depending of the intensity of the rainfall (difficult to calibrate)	
	Immediate equilibrium between rainwater and soil pore water	Not verified	
Mechanistic model	Immediate equilibrium between rainwater and soil pore water	Not verified	
	Site-specific (hydraulic gradient, etc) data for calibrating parameters	Site-specific data not easily available	

The choice of the best approach for the 2-FUN model is essentially guided by the availability of data required for the calibration of modelling parameters. A mechanistic model would thus lead to the collection of site-specific data that would be poorly available for the future end-users of the 2-FUN model. The second approach (“constant rainwater running off to rivers”) is based on some assumptions which were poorly verified and thus some parameters (e.g. Fraction of rainwater reaching freshwater systems) seem difficult to calibrate.

In conclusion, the use of a transfer function directly relating atmospheric deposits and freshwater contamination over short-term and long-term periods appears to be a good approach to simulate inputs to freshwater in a multimedia modelling system, even if it is empirical and calibrated only for a limited set of substances. This latter limit can however be overcome because the values of parameters required by this approach highly depend on the distribution of the substance between pore water and soil particles (Joshi et Shukla, 1991) and thus inter-substances extrapolation can be envisioned.

3.5 The biota contamination

This section intends to provide elements for answering to the questions 2.d, 2.e, 2.k, 2.l:
how many species for representing biological compartments of interest for humans?
is it necessary to develop a food-web model to simulate the transfer to fish?
is it sufficient to consider an equilibrium bioconcentration factor or is it necessary to incorporate also kinetic elimination/clearance rates ?
is it sufficient to consider direct transfer from water or is it necessary to include food intake routes ?

Two main approaches were identified in the previous review of the existing models:

- the first approach is based on a exhaustive description of the main taxonomic (e.g. algae, invertebrates, fish, benthos, etc) or functional groups (e.g. primary producers, primary consumers, decomposers, etc) present in the freshwater system and on their relationships. The parameterisation of such models requires information on direct bioconcentration from water intake for each group, as well as information on its diet (food-related contamination). Such

models are developed essentially when the target is not only human risk assessment, but also ecological risk assessment;

- the second approach considers one single compartment for representing freshwater biota, i.e. fish, because this latter is assumed to be the only compartment of interest for human intake. The transfer from water to biota (fish) is thus simulated by one single parameter (a Bioconcentration factor) under steady-state hypothesis or by two parameters (a Bioconcentration factor and an elimination rate) if kinetics are taken into account.

Some studies showed that the food chain exposure may constitute significant exposure routes for some pollutants (e.g. Carbone et al, 2000). However, models incorporating food web introduce significant parameter uncertainties: bioconcentration factors are scarcely available for some intermediate compartments (indeed, the experimental endpoints studied for compartments such as invertebrates or benthic organisms are generally toxicity endpoints rather than 'bioaccumulation' endpoints) and diet parameters must also be defined.

Besides, many bioaccumulation factors (BAFs) possibly used for the parameterisation of multimedia models are originated from field measurements and thus implicitly include uptake from food and water, though water is identified as the explicit source (through the ratio concentration in biota/concentration in water)⁵. This presumes that the concentration in the food item is relatively constant relative to the concentration in water. Consequently, the incorporation of food routes in the contamination of fish depends more on the choice of parameter values (which can implicitly include food item according to the conditions under which they were determined) rather than on the complexity of the mathematical description of the model.

In conclusion, for the 2-FUN model, it is recommended not to consider intermediate food compartments leading to contamination of fish (the compartment of concern for human intake).

However, for some contaminants (e.g. mercury), significant differences in the contamination of fish are observed according their food composition, carnivorous fish being more contaminated because of biomagnification. In order to be able to account for this latter process for some pollutants, it is suggested to distinguish two compartments for representing biota in freshwater, more precisely herbivorous fish and carnivorous fish respectively. For herbivorous fish, a special attention is however required to select relevant parameter values, i.e. those implicitly incorporating food routes even if waterborne exposure is explicitly identified as the main exposure route.

An other question regards steady-state models vs kinetic models. Steady-state models assume that the concentration in fish is immediately equilibrated with concentration in freshwater, while kinetic models considers a depuration rate in fish. The consequence of steady-state models is that fish contamination is not dependent of past contamination events in water; this is not relevant according to several experimental observations showing that fishes remain contaminated even after a long period following a pollution event (e.g. Gobas and Mackay, 1987; Peles et al, 2000; Kooijman et al, 2004). Such experimental observations underline the importance to take into account retention processes of contaminants in fish after pollution events (especially if these events are intermittent and lead to high temporal variations in the water contamination) and thus the relevance to introduce into the model an elimination kinetic rate in fish tissues. It is thus concluded that the 2-FUN model will incorporate kinetic depuration process in its conceptual architecture.

[3.6 Processes of transformation](#)

This section intends to provide elements for answering to the questions Question 2.h: is it sufficient to use a 'global' degradation rate implicitly including several degradation processes?
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⁵ Both Bioconcentration Factors (BCF) and Bioaccumulation Factors (BAF) are calculated as the ratio, at equilibrium, of biota concentration to water concentration. Although the calculation of BCF and BAF are usually the same, the interpretations are slightly different, accumulation arising from water only for BCF and from water and food for BAF. Consequently, BAF are generally derived from field measurements, while BCF is measured under laboratory conditions (McGeer et al, 2003)

Several processes may be responsible for the transformation of organic pollutants in the natural environment: hydrolysis, photolysis, microbial degradation. However, the modelling of each of these processes is relevant only if co-factors are available (e.g. light intensity for photolysis, etc). Thus, it is suggested to use a global degradation rate (as done in most of the reviewed models) to describe the transformation processes without distinguishing each of them.

3.7 The 2-FUN Interaction Matrix for the freshwater system

The 2-Fun Interaction matrix for freshwater system (Figure 8) was built by taking into account the analysis previously detailed.

Atmosphere Gas			Dry and wet deposition Absorption					
	Atmosphere Aerosols	Dry and wet deposition	Dry and wet deposition					
		Soil surface	Erosion-runoff					
Volatilization			River/lake water Dissolved phase	Adsorption		Bioaccumulation	Bioaccumulation	Physico-chemical and biological degradation
			Desorption	River/lake water Suspended particulate Matter	Particles deposition			
				Particles resuspension	Water diffusion			
				Pore water diffusion	Bottom sediments			
						Herbivorous fish	Biomagnification	Biological elimination Degradation
							Carnivorous fish	Biological elimination Degradation
								Sink

Figure 9 - The 2-FUN Interaction Matrix for the surface freshwater sub-system

The main principles of this conceptual model are summarised below:

<ul style="list-style-type: none"> The water column was subdivided in two sub-compartments (dissolved and particulate phases respectively). An equilibrium was assumed between these two phases through the use of a partition (or distribution) coefficient. 	<table border="1"> <tr> <td>River/lake water Dissolved phase</td> <td>Adsorption</td> </tr> <tr> <td>Desorption</td> <td>River/lake water Suspended particulate Matter</td> </tr> </table>	River/lake water Dissolved phase	Adsorption	Desorption	River/lake water Suspended particulate Matter					
River/lake water Dissolved phase	Adsorption									
Desorption	River/lake water Suspended particulate Matter									
<ul style="list-style-type: none"> Physical exchanges (deposition/resuspension of particles) of contaminants between the water column and the bottom sediment were simulated. A dynamic model incorporating the effect of flow rates on deposition and resuspension processes was preferred to realistically describe the dynamics of sediments and avoid the use of 'burial' process. 	<table border="1"> <tr> <td>River/lake water Suspended particulate Matter</td> <td>Particles deposition</td> </tr> <tr> <td>Particles resuspension</td> <td>Bottom sediments</td> </tr> </table>	River/lake water Suspended particulate Matter	Particles deposition	Particles resuspension	Bottom sediments					
River/lake water Suspended particulate Matter	Particles deposition									
Particles resuspension	Bottom sediments									
<ul style="list-style-type: none"> Diffusive transfer at the water-sediment interface was included in the 2-FUN conceptual model. However, only a generic approach (similar to those included in other multimedia models) was used as a screening method. 	<table border="1"> <tr> <td>River/lake water Suspended particulate Matter</td> <td>Water diffusion</td> </tr> <tr> <td>Pore water diffusion</td> <td>Bottom sediments</td> </tr> </table>	River/lake water Suspended particulate Matter	Water diffusion	Pore water diffusion	Bottom sediments					
River/lake water Suspended particulate Matter	Water diffusion									
Pore water diffusion	Bottom sediments									
<ul style="list-style-type: none"> Dry deposition of pollutants associated to aerosols was simulated through a constant deposition velocity of the aerosols particles. <p>Wet deposition of aerosols was simulated by a scavenging ratio describing the entrainment of pollutants associated to aerosols during rain events.</p>	<table border="1"> <tr> <td>Atmosphere Aerosols</td> <td colspan="2">Dry and wet deposition</td> </tr> <tr> <td></td> <td>River/lake water Dissolved phase</td> <td></td> </tr> <tr> <td></td> <td></td> <td>River/lake water Suspended particulate Matter</td> </tr> </table>	Atmosphere Aerosols	Dry and wet deposition			River/lake water Dissolved phase				River/lake water Suspended particulate Matter
Atmosphere Aerosols	Dry and wet deposition									
	River/lake water Dissolved phase									
		River/lake water Suspended particulate Matter								

- Dry deposition of vapour-phase pollutants was simulated through a constant deposition velocity calculated through an analogy to electrical resistance.

Wet deposition of gas was simulated by a scavenging ratio describing the entrainment of pollutants associated to gaseous phase during rain events.

Absorption/volatilisation of semi-volatile substances at the air-freshwater interface was modelled using the stagnant boundary theory (two-film model), the pollutant being assumed to diffuse across two layers (stagnant water layer and stagnant air layer) characterised by two resistances in series.

Atmosphere	Dry and wet deposition	
Gas	Absorption	
Volatilization	River/lake water	
	Dissolved phase	
		River/lake water
		Suspended particulate Matter

- Inputs from erosion-runoff of contaminated soils was taken into account through the use of a kinetic transfer function directly relating atmospheric deposits and freshwater contamination over short-term and long-term periods.

Atmosphere	Dry and wet deposition		
	Soil surface	Erosion-runoff	
		River/lake water	
		Dissolved phase	
			River/lake water
			Suspended particulate Matter

- Two single compartments for representing biota in freshwater, more precisely herbivorous fish and carnivorous respectively, were considered. The contamination of fish through food routes was not explicitly described, water being the explicit source of contamination. However, it is suggested to parameterise the model with bioaccumulation factors (BAF) which implicitly include uptake from food and water. For carnivorous fish, a biomagnification factor is added.

River/lake water	Bioaccumulation	Bioaccumulation
Dissolved phase	Herbivorous Fish	Biomagnification
		Carnivorous fish

- The 2-FUN model incorporated kinetic depuration process for fish to represent retention processes of contaminants in fish after pollution events.

Fish	Biological elimination
	Sink

- A global degradation rate was used to describe the transformation processes of organics without distinguishing each of them (hydrolysis, photolysis, microbial degradation).

River/lake water			Physico-chemical and biological degradation
Dissolved phase			
	River/lake water		
	Suspended particulate Matter	Bottom sediments	
		Fish	
			Degradation
			Sink

4. THE SURFACE FRESHWATER SYSTEM - DEFINITION OF THE MATHEMATICAL 2-FUN MODEL

The objective of this section is to describe the mathematical ‘translation’ of the conceptual architecture previously detailed. Time-dependent pollutant concentration of each of the freshwater subcompartment (i.e. dissolved phase, suspended particulate matter, bottom sediments and fish) was derived from inputs/outputs/transformation processes previously selected and mathematically described in the present section, according a mass-balance system.

4.1 Inputs/outputs into the freshwater system

4.1.1 Inputs from upstream river flux and from internal discharges

In the 2-FUN model, the concentration of upstream inputs to the investigated river section is assumed to be known. We noted $C_{rw_upstream}$ (in $mg.m^{-3}$) the concentration in raw river/lake freshwater due to upstream fluxes.

$C_{rw_upstream}$ may be given by dispersion models simulating the transport of pollutants from their release point in the river to the input point of the investigated region, or by monitoring data.

Point-source discharges occurring within the investigated region (i.e. the investigated box) can also be considered as sources of contamination in the freshwater system. Such discharges (expressed in $mg.d^{-1}$) are diluted in the flow rate of the river, leading to a variation in raw water concentration:

$$(1) \quad C_{rw_point_sources}(t) = \frac{D_{point_sources}(t)}{86400.Q(t)}$$

where :

- ✓ $C_{rw_point_sources}(t)$ ($mg.m^{-3}$): concentration in raw river water due to point-source discharges into the freshwater system;
- ✓ $D_{point_sources}(t)$ ($mg.d^{-1}$): time-dependent flux of pollutant into the freshwater system from point sources (e.g. industry);
- ✓ $Q(t)$ ($m^3.s^{-1}$): time-dependent flow rate of the river.

4.1.2 Inputs from dry deposition of aerosols

The dry deposition of pollutants present in the atmosphere under particulate can be modelled by considering a constant dry deposition velocity. Thus:

$$(2) \quad \frac{dC_{rw_dry_dep}}{dt} = v_{dry,atm} \cdot \frac{C_{part,atm} \cdot TSP_{atm}}{h_{fw}}$$

where:

- ✓ $\frac{dC_{rw_dry_dep}}{dt}$ ($mg.m^{-3}.d^{-1}$): kinetic variation in the concentration in raw river water due to dry deposition of atmospheric particles;
- ✓ $C_{part_atm}(t)$ ($mg.g^{-1}$): time-dependent concentration of particulate pollutant in the atmosphere;
- ✓ TSP_{atm} ($g.m^{-3}$): total suspended particles (aerosols) in the atmosphere.
- ✓ h_{fw} (m): depth of the river;
- ✓ $v_{dry,atm}$ ($m.d^{-1}$): dry deposition velocity of particles.

Moreover, the partition of pollutant in the atmosphere between aerosols and gas is described by a partition coefficient $K_{p,atm}$ and, as a consequence:

$$(3) \quad C_{part_atm}(t) = \frac{K_{p,atm} \cdot C_{atm}(t)}{1 + K_{p,atm} \cdot TSP_{atm}}$$

where :

- ✓ $C_{atm}(t)$ ($mg.m^{-3}$): time-dependent total concentration of pollutant in the atmosphere;
- ✓ $K_{p,atm}$ ($m^3.g^{-1}$): partition coefficient between aerosols and gaseous forms in the atmosphere⁶;

⁶ A discussion on the descriptors of the partition coefficient $K_{p,atm}$ is detailed in the Deliverable related to the Air system (Deliverable D2.5).

We thus obtain :

$$(4) \quad \frac{dC_{rw,dry_dep}}{dt} = v_{dry,atm} \cdot \frac{K_{p,atm} \cdot C_{atm}(t)}{1 + K_{p,atm} \cdot TSP_{atm}} \cdot \frac{TSP_{atm}}{h_{fw}}$$

4.1.3 Inputs from wet deposition of gaseous pollutants and aerosols

The wet deposition of pollutants present in the atmosphere under particulate or gaseous forms can be modelled by considering that a constant fraction of pollutant is washed out in rainwater during precipitations. Thus:

$$(5) \quad \frac{dC_{rw,wet_dep,part}}{dt} = \Lambda_{part} \cdot Rain(t) \cdot \frac{C_{part,atm} \cdot TSP_{atm}}{h_{fw}}$$

and

$$(6) \quad \frac{dC_{rw,wet_dep,gas}}{dt} = \Lambda_{gas} \cdot Rain(t) \cdot \frac{C_{gas,atm}}{h_{fw}}$$

where :

- ✓ $\frac{dC_{rw,wet_dep,part}}{dt}$ ($mg \cdot m^{-3} \cdot d^{-1}$): kinetic variation in the concentration in raw river water due to wet deposition of particles;
- ✓ $\frac{dC_{rw,wet_dep,gas}}{dt}$ ($mg \cdot m^{-3} \cdot d^{-1}$): kinetic variation in the concentration in raw river water due to wet deposition of gaseous pollutants (rain dissolution);
- ✓ $C_{part_atm}(t)$ ($mg \cdot g^{-1}$): time-dependent concentration of particulate pollutant in the atmosphere;
- ✓ $C_{gas_atm}(t)$ ($mg \cdot m^{-3}$): time-dependent concentration of gaseous pollutant in the atmosphere;
- ✓ $Rain(t)$ ($m \cdot d^{-1}$): time-dependent rainfall ;
- ✓ h_{fw} (m): depth of the river;
- ✓ Λ_{part} (-) : rainfall scavenging ratio for particles (i.e. ratio between the concentration in rainwater (in $mg \cdot m^{-3}$ rainfall) and in the particles ($mg \cdot m^{-3}$ air) respectively);
- ✓ Λ_{gas} (-) : rainfall scavenging ratio for gas (i.e. ratio between the concentration in rainwater (in $mg \cdot m^{-3}$ rainfall) and in gas ($mg \cdot m^{-3}$ air) respectively);
- ✓ TSP_{atm} ($g \cdot m^{-3}$ air): total suspended particles (aerosols) in the atmosphere.

Moreover, the partition of pollutant in the atmosphere between aerosols and gas is described by a partition coefficient $K_{p,atm}$ and, as a consequence:

$$(7) \quad C_{gas_atm}(t) = \frac{C_{atm}(t)}{1 + K_{p,atm} \cdot TSP_{atm}}$$

where:

- ✓ $C_{\text{atm}}(t)$ ($\text{mg}\cdot\text{m}^{-3}$): time-dependent total concentration of pollutant in the atmosphere;
- ✓ $K_{\text{p,atm}}$ ($\text{m}^3\cdot\text{g}^{-1}$): partition coefficient between aerosols and gaseous forms in the atmosphere⁷;
- ✓ TSP_{atm} ($\text{g}\cdot\text{m}^{-3}$): total suspended particles (aerosols) in the atmosphere.

The combination of equations (5) to (7) gives:

$$(8) \quad \frac{dC_{\text{rw,wet_dep,part}}}{dt} = \Lambda_{\text{part}} \cdot \text{Rain}(t) \cdot \frac{K_{\text{p,atm}} \cdot \text{TSP}_{\text{atm}}}{h_{\text{fw}} \cdot (1 + K_{\text{p,atm}} \cdot \text{TSP}_{\text{atm}})} \cdot C_{\text{atm}}(t)$$

and

$$(9) \quad \frac{dC_{\text{rw,wet_dep,gas}}}{dt} = \Lambda_{\text{gas}} \cdot \text{Rain}(t) \cdot \frac{1}{h_{\text{fw}} \cdot (1 + K_{\text{p,atm}} \cdot \text{TSP}_{\text{atm}})} \cdot C_{\text{atm}}(t)$$

4.1.4 Inputs/outputs from diffusion of gaseous atmospheric pollutants⁸

Absorption/volatilization of semi-volatile substances at the air-freshwater interface was modelled using the stagnant boundary theory (two-film model), the pollutant being assumed to diffuse across two layers (stagnant water layer and stagnant air layer) characterized by two resistances in series. According to this approach, the net flux from freshwater to the atmosphere is driven by the fugacity difference between air and surface water:

$$(10) \quad F_{\text{fw-atm}}(t) = D_{\text{fw-atm}} \left(C_{\text{gas_atm}}(t) - \frac{H \cdot C_{\text{riv,dis}}(t)}{RT} \right)$$

where:

- ✓ $F_{\text{fw-atm}}(t)$ ($\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$): time-dependent net flux of the pollutant at the freshwater-atmosphere interface;
- ✓ $D_{\text{fw-atm}}$ ($\text{m}\cdot\text{d}^{-1}$): gas-phase overall mass transfer coefficient;
- ✓ $C_{\text{gas_atm}}(t)$ ($\text{mg}\cdot\text{m}^{-3}$): time-dependent concentration of gaseous pollutant in the atmosphere;
- ✓ $C_{\text{riv,dis}}(t)$ ($\text{mg}\cdot\text{m}^{-3}$): time-dependent concentration of the pollutant in dissolved river water;
- ✓ H ($\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$): Henry's law constant;
- ✓ R ($8.205 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$): universal gas constant;
- ✓ $T(t)$ (K): time-dependent temperature at the air-water interface.

The term $\frac{H \cdot C_{\text{riv,dis}}(t)}{RT}$ in equation (10) represents the gaseous concentration of the substance in river water, assumed to be in equilibrium with the dissolved concentration. This equilibrium is simulated by the adimensional Henry's law constant.

⁷ A discussion on the descriptors of the partition coefficient $K_{\text{p,atm}}$ is detailed in in the Deliverable related to the Air system (Deliverable D2.5).

⁸ This section is relevant only for non dissociated organics.

The gas-phase overall mass transfer coefficient is related to mass transfer coefficients for the liquid and gas films in series, as follows:

$$(11) \quad \frac{1}{D_{fw-atm}} = \frac{1}{D_{fw-atm,g}} + \frac{H}{RT \cdot D_{fw-atm,w}}$$

where:

- ✓ $D_{fw-atm,g}$ ($m \cdot d^{-1}$): gas film mass transfer coefficient;
- ✓ $D_{fw-atm,w}$ ($m \cdot d^{-1}$): liquid film mass transfer coefficient.

Besides, the concentrations in the dissolved phase of freshwater is given by:

$$(12) \quad C_{riv,dis}(t) = C_{rw}(t) \cdot \left(\frac{1}{1 + K_{d,w} \cdot SPM(t)} \right)$$

where:

- ✓ $C_{riv,dis}(t)$ ($mg \cdot m^{-3}$): time-dependent concentration of the pollutant in dissolved river water;
- ✓ $SPM(t)$ ($g \cdot m^{-3}$): time-dependent suspended matter concentration;
- ✓ $K_{d,w}$ ($m^3 \cdot g^{-1}$): distribution coefficient of the pollutant at the interface water-SPM⁹.

Moreover, the partition of pollutant in the atmosphere between aerosols and gas is described by a partition coefficient $K_{p,atm}$ (see equations (7)).

Thus, Equation (10) becomes:

$$(13) \quad F_{fw-atm}(t) = \frac{RT \cdot D_{fw-atm,g} \cdot D_{fw-atm,w}}{RT \cdot D_{fw-atm,w} + H \cdot D_{fw-atm,g}} \left[\frac{C_{atm}(t)}{1 + K_{p,atm} \cdot TSP_{atm}} - \frac{H}{RT} \cdot C_{rw}(t) \cdot \left(\frac{1}{1 + K_{d,w} \cdot SPM(t)} \right) \right]$$

The temporal variation of raw river water due to inputs from absorption/volatilization of gaseous pollutant can thus be calculated as follows:

$$(14) \quad \frac{dC_{rw,diff-atm}}{dt} = \frac{F_{fw-atm}(t)}{h_{fw}}$$

where :

- ✓ $C_{rw}(t)$ ($mg \cdot m^{-3}$): time-dependent concentration of the pollutant in raw river water;
- ✓ h_{fw} (m): depth of the river.

4.1.5 Inputs from erosion-runoff of contaminated soils

⁹ A discussion on the $K_{d,w}$ parameter is provided in section 4.2.1.

The model proposed for describing erosion/runoff of pollutants deposited on soils at a watershed scale is taken from works conducted in Europe and the United States after the bombogenic radioactive pulses and the Chernobyl accident, which represented unique case studies to experimentally measure in the field transfer of pollutants from contaminated soils to rivers (e.g. Linsley et al, 1982; Helton et al, 1985; Monte, 1995; Smith et al, 2000; Monte, 2004).

In particular, the following model was proposed to simulate the input of pollutants into a river after a pulse deposit (at time $t=0$) at a watershed scale (see Garcia-Sanchez, 2007):

$$(15) \quad \lambda_{\text{wash-off}}(t) = f_{\text{short_wash-off}} \lambda_{\text{short_wash-off}} \cdot \exp(-\lambda_{\text{short_wash-off}} \cdot t) + (1 - f_{\text{short_wash-off}}) \lambda_{\text{long_wash-off}} \cdot \exp(-\lambda_{\text{long_wash-off}} \cdot t)$$

where:

- ✓ $f_{\text{short_wash-off}}$ (-): fraction of deposited contamination affected by short-term (rapid) wash-off;
- ✓ $f_{\text{long_wash-off}}$ (-): fraction of deposited contamination affected by long-term (slow) wash-off;
- ✓ $\lambda_{\text{short_wash-off}}$ (d^{-1}): rapid wash-off rate constant (few weeks);
- ✓ $\lambda_{\text{long_wash-off}}$ (d^{-1}): slow wash-off rate constant (few years);
- ✓ $\lambda_{\text{wash-off}}(t)$ (d^{-1}): wash off rate constant at time t after the pulse deposit.

This model assumes that runoff/erosion (called here wash-off) occurs at two different time scales:

- wash-off is particularly intense during and within few weeks after deposition. This stage is referred as short-term wash-off. Short-term liquid wash-off originates in non-equilibrium sorption on the soil surface during wet deposition, the excess contamination being rapidly exported with runoff;
- wash-off is significantly lower for larger delays after deposition, but is still active years and decades after deposition. This stage is referred as long-term wash-off. Long-term liquid wash-off results from dilution of soil water with runoff water, and desorption from a thin soil layer. Availability of the radionuclide to liquid wash-off generally decreases with time, because of migration in deeper soil layers and ageing effect limiting desorption.

The half life of pollutants deposited in the watershed before their introduction in the freshwater system ($\lambda_{\text{wash-off}}(t)$) is thus calculated by combining short-term and long-term half lives respectively and their respective contribution to the wash off process.

For a pulse deposit occurring at time t_0 in the watershed, the wash-off flow rate at time t ($\Phi_{\text{wash-off}}(t)$) into the freshwater system is calculated as follows:

$$(16) \quad \Phi_{\text{wash-off}}(t) = D_{\text{soil}}(t_0) \cdot S_{\text{watershed}} \cdot \lambda_{\text{wash-off}}(t - t_0)$$

where:

- ✓ $\Phi_{\text{wash-off}}(t)$ ($mg \cdot d^{-1}$): wash-off flow rate entering into freshwater system the at time t ;
- ✓ $D_{\text{soil}}(t_0)$ ($mg \cdot m^{-2}$): deposit flux on the soil surface at time t_0 ;
- ✓ $S_{\text{watershed}}$ (m^2): surface of the watershed influencing the region under investigation.

This approach (experimentally tested and calibrated for pulse deposits such as nuclear bomb tests or Chernobyl) can be extended for chronic deposits assuming a superposition principle. Thus, if the watershed is submitted to continuous atmospheric deposition rates D_{soil} ($mg \cdot m^{-2} \cdot s^{-1}$), the wash-off flow rate at time t ($\Phi_{\text{wash-off}}(t)$) into the freshwater system is then:

$$(17) \quad \Phi_{\text{wash-off}}(t) = S_{\text{watershed}} \cdot \int D_{\text{soil}}(\tau) \lambda_{\text{wash-off}}(\tau - t) \cdot d\tau$$

where:

- ✓ $\Phi_{\text{wash-off}}(t)$ ($\mu\text{g}\cdot\text{d}^{-1}$): wash-off flow rate entering into freshwater system the at time t ;
- ✓ $D_{\text{soil}}(\tau)$ ($\mu\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$): deposit flux on the soil surface at time τ .

The temporal variation of raw river water due to inputs from runoff/erosion of contaminated soils at the watershed scale can thus be calculated as follows:

$$(18) \quad \frac{dC_{\text{rw,wash-off}}}{dt} = \frac{\Phi_{\text{wash-off}}(t)}{V_{\text{river-elt}}}$$

where:

- ✓ $V_{\text{river-elt}}(t)$ (m^3): volume of the freshwater system.

4.2 The inter-compartment transfers within the freshwater system

4.2.1 Interactions at the water-particles interface

The distribution of pollutants between water and suspended particulate matter (SPM) is supposed to be equilibrated and may be described by a “Distribution coefficient” $K_{\text{d,w}}$, representing the ratio between the particulate concentration (in $\text{mg}\cdot\text{g}^{-1}$) and the dissolved concentration (in $\text{mg}\cdot\text{m}^{-3}$).

Consequently, the concentrations in the dissolved and particulate phases respectively are given by:

$$(19) \quad C_{\text{riv,dis}}(t) = C_{\text{rw}}(t) \cdot \left(\frac{1}{1 + K_{\text{d,w}} \cdot \text{SPM}(t)} \right)$$

and

$$(20) \quad C_{\text{SPM}}(t) = C_{\text{rw}}(t) \cdot \left(\frac{K_{\text{d,w}}}{1 + K_{\text{d,w}} \cdot \text{SPM}(t)} \right)$$

where:

- ✓ $C_{\text{riv,dis}}(t)$ ($\text{mg}\cdot\text{m}^{-3}$): time-dependent concentration of the pollutant in dissolved river water;
- ✓ $C_{\text{SPM}}(t)$ ($\text{mg}\cdot\text{g}^{-1}$): time-dependent concentration of the pollutant in SPM at time interval n ;
- ✓ $\text{SPM}(t)$ ($\text{g}\cdot\text{m}^{-3}$): time-dependent suspended matter concentration;
- ✓ $K_{\text{d,w}}$ ($\text{m}^3\cdot\text{g}^{-1}$): distribution coefficient of the pollutant at the interface water-SPM.

The relationships (19) and (20) require the calculation of the time-dependent Suspended Particulate Matter (SPM(t)). As SPM concentration may highly depend on the hydrological conditions of the river, particularly during flood events, a relationship between the SPM concentration and the daily flow rate $Q_{\text{river}}(t)$ of the river is considered in the model:

$$(21) \quad \text{SPM}(t) = a \cdot Q^b(t)$$

where:

- ✓ a and b are empirical calibration parameters¹⁰;
- ✓ SPM(t) (g m⁻³): time-dependent suspended matter concentration;
- ✓ Q(t) (m³.s⁻¹): time-dependent flow rate of the river.

For metals, the distribution coefficient is an empirical parameter which can be derived from direct field measurements.

For neutral organics¹¹ (non dissociated organics for which lipophilic interactions are predominant), the distribution coefficient can be derived from the octanol-water partition coefficient and the organic matter content of SPM:

$$(22) \quad K_{d,w} = 10^{-6} \cdot y_{OC,SPM} \cdot 10^{\alpha_0 + \alpha_1 \cdot \log(K_{OW})}$$

where :

- ✓ $y_{OC,SPM}$ (-) : massic organic fraction in SPM;
- ✓ K_{OW} (-): octanol-water partition coefficient;
- ✓ α_0 and α_1 (-) : parameters of the linear relationship relating $\log(K_{OW})$ and $\log(K_{OC})$ (octanol-carbon partition coefficient).

For compounds able to be dissociated, direct relationship to octanol-water partition coefficient can not be used because ionic compounds may interact with ionic surfaces in a mode different from conventional hydrophobic sorption. Knowledge is then needed about their PK_a that drives the pH-dependent fractions of neutral and ionic components (for both acids and bases), and about the sorption/accumulation of both compound fractions into organic material. A first step could be to focus on Henderson-Hasselbalch equation, and analyze existing data in terms of neutral and ionic compound fractions. Surrogate studies could also be used to estimate membrane/water partition coefficients for the dissociated fraction¹².

4.2.2 Physical dynamics of particles between water column and bottom sediments

4.2.2.1. Mathematical model

Modelling of the deposition and erosion of fine cohesive particles (and associated pollutants) is generally based on the assumption that the bed shear stress exerted by the flow plays the dominant role. Several approaches were developed for simulating the deposition and erosion fluxes of particles (e.g. Krone, 1962; Partheniades, 1965; Mehta, 1988; Chapalain, 1992; Sanford and Maa, 2001), most of them being based on two main sediment characteristics: the critical shear stress of resuspension (stress at which initiation of erosion first occurs) and the critical shear stress of deposition (stress at which initiation of deposition first occurs).

In the 2-FUN model, the approaches proposed by Krone (1962) and Partheniades (1965) were selected because they were used in a wide range of contexts (e.g. Ciffroy et al, 2000, Liu et al, 2002, El Ganaoui et al, 2004):

- deposition is assumed to occur only when the bed shear stress τ is lower than a critical value (the critical deposition shear stress τ_d), i.e. when the flow velocity v_{flow} is lower than a critical value (the critical flow velocity for deposition $v_{flow,d}$). If such a condition is verified, the flux of particulate deposition F_d (in g m⁻² s⁻¹) is given by the following relation:

¹⁰ If the end-user prefers to use a constant mean SPM concentration, b may be put equal to zero and a is the mean SPM concentration.

¹¹ i.e. Dissociation of an organic acid or base can affect its interaction with solids. This relationship is valid for substances satisfying the following condition: $\frac{1}{1 + 10^{pK_a - pH}} \approx 1$ (non dissociated fraction close to one)

¹² This issue will be illustrated more in detail in D4.3.

$$(23) \quad F_d(t) = W_c \cdot \text{SPM}(t) \cdot \left(1 - \frac{v_{\text{flow}}(t)}{v_{\text{flow}_d}}\right) \quad \text{if } v_{\text{flow}} < v_{\text{flow}_d}$$

$$F_d(t) = 0 \quad \text{if } v_{\text{flow}} \geq v_{\text{flow}_d}$$

where:

- ✓ $F_d(t)$ ($\text{g m}^{-2} \text{d}^{-1}$): time-dependent deposition flux of particles ;
- ✓ $v_{\text{flow}}(t)$ (m.s^{-1}): time-dependent flow velocity;
- ✓ v_{flow_d} (m.s^{-1}): critical flow velocity for deposition;
- ✓ W_c (m d^{-1}): settling velocity of particles;
- ✓ $\text{SPM}(t)$ (g m^{-3}): time-dependent suspended matter concentration.

- resuspension is assumed to occur only when the bed shear stress τ is higher than a critical value (the critical resuspension shear stress τ_r), i.e. when the flow velocity v_{flow} is higher than a critical value (the critical flow velocity for resuspension v_{flow_r}). If such a condition is verified (and if sediments are present), the flux of particulate resuspension F_r (in $\text{g m}^{-2} \text{s}^{-1}$) is given by the following relation:

$$(24) \quad F_r(t) = e \cdot \left(1 - \frac{v_{\text{flow}}(t)}{v_{\text{flow}_r}}\right) \quad \text{if } v_{\text{flow}} > v_{\text{flow}_r} \quad (\text{negative flux from sediments to water column})$$

column)

$$F_r(t) = 0 \quad \text{if } v_{\text{flow}} \leq v_{\text{flow}_r}$$

where:

- ✓ $F_r(t)$ ($\text{g m}^{-2} \text{d}^{-1}$): resuspension flux of particles ;
- ✓ v_{flow_r} (m.s^{-1}): critical flow velocity for resuspension (obviously, $v_{\text{flow}_r} > v_{\text{flow}_d}$);
- ✓ e ($\text{g m}^{-2} \text{d}^{-1}$): erosion rate.

The flow velocity v_{flow} can be calculated by using the flow rate of the river and its section:

$$(25) \quad v_{\text{flow}}(t) = \frac{Q(t)}{h_{\text{fw}} \cdot l_{\text{fw}}}$$

where:

- ✓ $v_{\text{flow}}(t)$ (m.s^{-1}): time-dependent flow velocity;
- ✓ $Q(t)$ ($\text{m}^3 \cdot \text{s}^{-1}$): time-dependent flow rate of the river.
- ✓ h_{fw} (m): depth of the river;
- ✓ l_{fw} (m): width of the river.

Generally, critical flow velocities for deposition (v_{flow_d}) and resuspension (v_{flow_r}) are not directly given in the literature, but critical deposition shear stress τ_d and critical resuspension shear stress τ_r . To connect these parameters, it is possible to use the following equations:

$$(26) \quad \tau_d = \rho \cdot g \cdot h_{\text{fw}} \cdot \frac{v_{\text{flow}_d}^2}{K_s^2 \cdot h_{\text{fw}}^{4/3}}, \text{ or} \quad v_{\text{flow}_d} = K_s \cdot \left(\frac{\tau_d \cdot h_{\text{fw}}^{1/3}}{\rho \cdot g} \right)^{1/3}$$

and

$$(27) \quad \tau_r = \rho \cdot g \cdot h_{fw} \cdot \frac{v_{flow-r}^2}{K_s^2 \cdot h_{fw}^{4/3}}, \text{ or} \quad v_{flow-r} = K_s \cdot \left(\frac{\tau_r \cdot h_{fw}^{1/3}}{\rho \cdot g} \right)^{1/3}$$

where:

- ✓ K_s ($m \cdot s^{-1}$): Strickler friction coefficient (-).

Besides, relationship (23) requires also the calculation of the time-dependent Suspended Particulate Matter (SPM(t)) (see section 4.2.1, equation(21)).

The concentration of bed sediments is thus given by:

$$(28) \quad \boxed{\text{Sed}(t) = \max\{0; \text{Sed}(t - dt) + F_{fw-sed}(t) \cdot dt\}}$$

where

$\text{Sed}(t)$ ($g \cdot m^{-2}$): concentration of particles in bottom sediments at time interval n.

The temporal variation of pollutant concentration in raw river water due to exchanges of contaminated particles between the water column and bottom sediments can thus be calculated as follows:

If $F_r(t) > 0$ (resuspension of sediments), then

$$(29) \quad \frac{dC_{rw, sed_phys}}{dt} = \frac{F_r(t)}{h_{fw}} \cdot C_{sed}(t)$$

If $F_d(t)=0$ and $F_r(t)= 0$ (nor deposition, nor resuspension of sediments), then

$$(30) \quad \frac{dC_{rw, sed_phys}}{dt} = 0$$

If $F_d(t) > 0$ (deposition of SPM), then

$$(31) \quad \frac{dC_{rw, sed_phys}}{dt} = - \frac{F_d(t)}{h_{fw}} \cdot \frac{K_{d,w}}{1 + K_{d,w} \cdot SPM(t)} \cdot C_{rw}(t)$$

where:

- ✓ C_{rw} ($mg \cdot m^{-3}$): concentration in raw river water;
- ✓ $K_{d,w}$ ($g \cdot m^{-3}$): distribution coefficient of the pollutant at the interface water-particles;
- ✓ $F_r(t)$ ($g \cdot m^{-2} \cdot d^{-1}$): resuspension flux of particles ;
- ✓ $F_d(t)$ ($g \cdot m^{-2} \cdot d^{-1}$): time-dependent deposition flux of particles ;
- ✓ h_{fw} (m): depth of the river;
- ✓ $SPM(t)$ ($g \cdot m^{-3}$): time-dependent suspended matter concentration;
- ✓ $C_{sed}(t)$ ($mg \cdot g^{-1}$): contaminant concentration in bottom sediments.

The mass-balance equations can also be derived for bottom sediments:

If $F_r(t) > 0$ (resuspension of sediments) and if $Sed(t) > 0$, then

$$(32) \quad \frac{dC_{sed}}{dt} = -F_r(t) \cdot \frac{C_{sed}(t)}{Sed(t)}$$

If $F_d(t) = 0$ and $F_r(t) = 0$ (nor deposition, nor resuspension of sediments), then

$$(33) \quad \frac{dC_{sed}}{dt} = 0$$

If $F_d(t) > 0$ (deposition of SPM), then

$$(34) \quad \frac{dC_{sed}}{dt} = F_d(t) \cdot \frac{K_{d,w}}{(1 + K_{d,w} \cdot SPM(t))} \cdot C_{rw}(t)$$

4.2.3 Diffusion of pollutants between water column and bottom sediments

The diffusion of contaminants at the interface surface water-sediment pore water is based on a two film diffusion description, where the transport into the sediment is assumed to happen through two layers of resistance: the first layer represents the laminar water-side film and the second one sediment-side boundary layer.

According to models already implemented in other tools (e.g. Brandes et al, 1996; Sørensen et al, 2001; Warren et al, 2007), the diffusive flux at the surface water-sediment interface can be simulated by taking into account the concentration gradient between the two compartments and a mass transfer factor:

$$(35) \quad F_{fw-sed,diff}(t) = D_{fw-sed,dif} \cdot (C_{riv,diss}(t) - C_{sed,pore_water}(t))$$

where :

- ✓ $F_{fw-sed,diff}(t)$ ($mg \cdot m^{-2} \cdot d^{-1}$): time-dependent flux of pollutant between surface water and sediment due to diffusion (negative value if the net flux is from sediment to river column);
- ✓ $D_{fw-sed,dif}$ ($m \cdot d^{-1}$): mass transfer coefficient at the 'surface water-sediment' interface ;
- ✓ $C_{riv,diss}(t)$ ($mg \cdot m^{-3}$): time-dependent concentration of the pollutant in dissolved river water ;
- ✓ $C_{sed,pore_water}(t)$ ($mg \cdot m^{-3}$): time-dependent concentration of the pollutant in pore water of the sediment.

It can be assumed that the main fraction of pollutants present in the sediment is associated to the particles and thus:

$$(36) \quad C_{sed,pore_water}(t) = \frac{C_{sed,particles}(t)}{K_{d,ses}} \approx \frac{C_{sed}(t)}{K_{d,ses}}$$

where :

- ✓ $C_{sed,particles}(t)$ ($mg \cdot g^{-1}$): time-dependent concentration of the pollutant in sediment particles ;

- ✓ $C_{sed}(t)$ ($mg \cdot g^{-1}$): time-dependent total concentration of the pollutant in sediment;
- ✓ $K_{d,sed}$ ($m^3 \cdot g^{-1}$): distribution coefficient of the pollutant at the interface 'pore water-sediment particles'.

By combining equation (19), (35) and (36), we obtain:

$$(37) \quad F_{fw-sed,diff}(t) = D_{fw-sed,dif} \cdot \left[C_{rw}(t) \cdot \left(\frac{1}{1 + K_{d,w} \cdot SPM(t)} \right) - \frac{C_{sed}(t)}{K_{d,sed}} \right]$$

where:

- ✓ $C_{rw}(t)$ ($mg \cdot m^{-3}$): concentration of the pollutant in raw river water;
- ✓ $SPM(t)$ ($g \cdot m^{-3}$): suspended matter concentration;
- ✓ $K_{d,w}$ ($m^3 \cdot g^{-1}$): distribution coefficient of the pollutant at the interface water-SPM;
- ✓ $K_{d,sed}$ ($m^3 \cdot g^{-1}$): distribution coefficient of the pollutant at the interface 'sediment pore water-sediment particles'.

The distribution coefficient at the interface sediment pore water-sediment particles is estimated in a similar way as for surface water:

- ✓ for metals, it is an empirical parameter which can be derived from direct field measurements;
- ✓ For neutral organics, it can be derived from the octanol-water partition coefficient and the organic matter content of sediment:

$$(38) \quad K_{d,sed} = 10^{-6} \cdot y_{OC,sed} \cdot 10^{\alpha_0 + \alpha_1 \cdot \log(K_{OW})}$$

where :

- ✓ $y_{OC,sed}$ (-) : massic organic fraction in sediments;
- ✓ K_{OW} (-): octanol-water partition coefficient;
- ✓ α_0 and α_1 (-) : parameters of the linear relationship relating $\log(K_{OW})$ and $\log(K_{OC})$ (octanol-carbon partition coefficient).

The mass transfer coefficient $D_{fw-sed,dif}$ at the surface water-sediment interface is estimated according to the assumption that it results from two resistances in series. Thus:

$$(39) \quad \frac{1}{D_{fw-sed,dif}} = \frac{\delta_w}{B_w} + \frac{\delta_{sed}}{B_{sed}}$$

where:

- ✓ δ_w (m) : boundary layer thickness below water;
- ✓ δ_{sed} (m) : boundary layer thickness above sediment;
- ✓ B_w ($m^2 \cdot d^{-1}$) : effective diffusivity of chemical in surface water ;
- ✓ B_{sed} ($m^2 \cdot d^{-1}$) : effective diffusivity of chemical in sediment.

The effective diffusivities in water and sediments can be estimated from diffusivity in pure water (Millington and Quirk, 1961):

$$(40) \quad B_w = B_{\text{pure_water}}$$

$$(41) \quad B_{\text{sed}} = \phi_{\text{sed}}^{(4/3)} \cdot B_{\text{pure_water}}$$

where:

- ✓ $B_{\text{pure_water}}$ ($\text{m}^2 \cdot \text{d}^{-1}$): diffusivity of pure water (typically $4 \cdot 10^{-6} \text{ m}^2 \cdot \text{h}^{-1}$, or $9.6 \cdot 10^{-5} \text{ m}^2 \cdot \text{d}^{-1}$);
- ✓ ϕ_{sed} (-): porosity of the sediment.

By combining the equations (37), (39), (40) and (41), we obtain:

$$(42) \quad F_{\text{fw-sed,diff}}(t) = \frac{B_w \cdot \phi_{\text{sed}}^{(4/3)}}{\delta_{\text{sed}} + \delta_w \cdot \phi_{\text{sed}}^{(4/3)}} \cdot C_{\text{rw}}(t) \cdot \left[\frac{1}{1 + K_{\text{d,w}} \cdot \text{SPM}(t)} - \frac{C_{\text{sed}}(t)}{K_{\text{d,sed}}} \right]$$

The temporal variation of raw river water due to diffusive exchanges of dissolved contaminant in surface water and sediment pore water respectively can thus be calculated as follows:

$$(43) \quad \frac{dC_{\text{rw, sed_diff}}}{dt} = - \frac{F_{\text{fw-sed,dif}}(t)}{h}$$

The mass-balance equations can also be derived for bottom sediments (if $\text{Sed}(t) > 0$):

$$(44) \quad \frac{dC_{\text{sed,diff}}}{dt} = \frac{F_{\text{fw-sed,phys}}(t)}{\text{Sed}(t)}$$

4.2.4 Uptake/elimination of pollutants by herbivorous fish

As proposed in section 3.5, water is identified as the explicit source for herbivorous fish contamination (even if uptake from food and water are implicitly included through a Bioaccumulation factor). Thus, the time-dependent concentration of pollutant in herbivorous fish is given by:

$$(45) \quad \frac{dC_{\text{herb_fish}}}{dt} = -\lambda_{\text{elimination_fish}} \cdot (\text{BAF}_{\text{fish}} \cdot C_{\text{riv,dis}}(t) - C_{\text{herb_fish}}(t))$$

where:

- ✓ $C_{\text{herb_fish}}(t)$ ($\text{mg} \cdot \text{g}^{-1} \text{ WW}$): time-dependent concentration of the pollutant in herbivorous fish;
- ✓ $C_{\text{riv,dis}}(t)$ ($\text{mg} \cdot \text{m}^{-3}$): time-dependent concentration of the pollutant in dissolved river water;
- ✓ $\lambda_{\text{elimination_fish}}$ (d^{-1}): elimination rate constant in fish ;
- ✓ BAF_{fish} ($\text{g WW} \cdot \text{m}^{-3}$): bioaccumulation factor for fish

For metals, the BAF parameter is an empirical parameter which can be derived from direct field measurements.

According to the 'hydrophobicity' model, which assumes that diffusive lipophilic interactions are predominant, (worst-case) BAF values were classically derived from the octanol-water partition coefficient for neutral organics:

$$(46) \quad \log \text{BAF}_{\text{fish}} = a \cdot \log K_{\text{ow}} - b$$

where :

- ✓ K_{ow} (-): octanol-water partition coefficient;
- ✓ a and b (-) : parameters of the linear relationship relating $\log(\text{BAF}_{\text{fish}})$ and $\log(K_{\text{ow}})$. a represents the suitability of octanol as a surrogate for the lipid compartment and b is the logarithm of the fish lipid content.

However, relationship (44) shows several exceptions:

- for more hydrophilic substances (low K_{ow}), the aqueous phase is not yet negligible in the exchanges at the water-membrane interface, resulting in higher BAF than those predicted by the 'hydrophobicity' model only;
- for superhydrophobic substances (typically $\log(K_{\text{ow}}) > 6$), deviations from the linear model were observed, with even decreasing BAFs when K_{ow} increases;
- because of the reduction of hydrophobicity upon dissociation or protonation, the linear model previously indicated should be adapted for ionizable compounds.

This is the reason why other models were proposed to incorporate mitigation factors (for a more detailed description, see Schuurman et al (2007)). The parameterization issue will be discussed in more detail in Deliverable 2.3.

4.2.5 Uptake/elimination of pollutants by carnivorous fish

The biomagnification process can be simulated for some substances for which there is an evidence of increasing concentrations over the food chain.

Thus, the time-dependent concentration of pollutant in carnivorous fish is given by:

$$(47) \quad \frac{dC_{\text{carn_fish}}}{dt} = -\lambda_{\text{elimination_fish}} \cdot (\text{BMF}_{\text{fish}} \cdot \text{BAF}_{\text{fish}} \cdot C_{\text{riv,dis}}(t) - C_{\text{carn_fish}}(t))$$

where:

- ✓ $C_{\text{carn_fish}}(t)$ ($\text{mg} \cdot \text{g}^{-1}$ WW) : time-dependent concentration of the pollutant in carnivorous fish;
- ✓ $C_{\text{riv,dis}}(t)$ ($\text{mg} \cdot \text{m}^{-3}$): time-dependent concentration of the pollutant in dissolved river water;
- ✓ $\lambda_{\text{elimination_fish}}$ (d^{-1}) : elimination rate constant in fish ;
- ✓ BAF_{fish} ($\text{g WW} \cdot \text{m}^{-3}$) : bioaccumulation factor for fish;
- ✓ BMF_{fish} (-) : biomagnification factor for carnivorous fish.

[4.3 The mass-balance model for the freshwater system](#)

4.3.1 Mass-balance model for raw river water

The kinetic variation in the quantity of contaminant in raw river water of the investigated system is given by:

(48)

$$\begin{aligned}
V_{\text{river}} \cdot \frac{dC_{\text{rw}}}{dt} = & \underbrace{\frac{D_{\text{point_sources}}(t)}{86400 \cdot Q(t)}}_{\text{point sources}} + \underbrace{Q(t) \cdot C_{\text{rw_upstream}}}_{\text{input from upstream}} - \underbrace{Q(t) \cdot C_{\text{rw}}(t)}_{\text{output to downstream}} + \underbrace{V_{\text{river}} \cdot \frac{dC_{\text{rw,dry_dep}}}{dt}}_{\text{input from dry particulate deposition}} + \underbrace{V_{\text{river}} \cdot \frac{dC_{\text{rw,wet_dep,part}}}{dt}}_{\text{input from wet particulate deposition}} + \\
& \underbrace{V_{\text{river}} \cdot \frac{dC_{\text{rw,wet_dep,gas}}}{dt}}_{\text{input from gaseous wet deposition}} + \underbrace{V_{\text{river}} \cdot \frac{dC_{\text{rw,diff_atm}}}{dt}}_{\text{input / output from diffusion of atmospheric gas}} + \underbrace{V_{\text{river}} \cdot \frac{dC_{\text{rw,wash-off}}}{dt}}_{\text{input from soil wash-off}} + \underbrace{V_{\text{river}} \cdot \frac{dC_{\text{rw,sed_phys}}}{dt}}_{\text{input / output from sediment deposition / resuspension}} + \\
& \underbrace{V_{\text{river}} \cdot \frac{dC_{\text{rw,sed_diff}}}{dt}}_{\text{input / output from sediment diffusion}}
\end{aligned}$$

The expressions of each of the inputs/outputs are given in the previous sections, i.e.:

- inputs from dry particulate deposition: equation (4);
- inputs from wet particulate deposition: equation (8);
- inputs from wet gaseous deposition: equation (9);
- inputs/outputs from diffusion of atmospheric gas: equation (14);
- inputs from soil wash-off: equation (18);
- inputs/outputs from sediment deposition/resuspension: equation (29) or (30) or (31);
- inputs from sediment diffusion: equation (43).

4.3.2 Mass-balance model for sediments

The kinetic variation in the quantity of contaminant in sediments of the investigated system is given by:

$$(49) \quad \frac{dC_{\text{sed}}}{dt} = \underbrace{\frac{dC_{\text{sed_phys}}}{dt}}_{\text{input / output from sediment deposition / resuspension}} + \underbrace{\frac{dC_{\text{sed,diff}}}{dt}}_{\text{input / output from sediment diffusion}}$$

The expressions of each of the inputs/outputs are given in the previous sections, i.e.:

- inputs/outputs from sediment deposition/resuspension: equation (32) or (33) or (34);
- inputs from sediment diffusion: equation (44).

4.3.3 Models for dissolved water and Suspended Particulate Matter

The concentration in dissolved river water and SPM are calculated from values obtained for raw river water using equations (19) and (20).

4.3.2 Mass-balance model for fish

The time-dependent concentration in fish is calculated using equation (45) and (47).

CONCLUSIONS

The work presented in this deliverable allowed to define a transparent approach for the review and analysis of existing models simulating the transfer of contaminants in freshwaters. The Interaction Matrix approach allowed indeed to visualise the subdivision of the environment chosen in each model, as well as the exchange processes which were taken into account.

The critical review of different structural models allowed to put in evidence the main differences among models and the critical issues for the construction of an homogeneous framework. Assumptions chosen for the 2-FUN model were thus discussed and justified in a transparent way, leading to the definition of the 2-FUN Interaction matrix for the freshwater sub-system.

The mathematical model, based on a mass-balance equation for each of the compartments of the freshwater system, was presented in detail. It will be implemented in the next future in a modelling software called Ecolego®. Ecolego® is a commercial product for simulation modelling of dynamic systems, developed by Facilia (<http://www.facilia.se/products/ecolego.asp>). An 'end-user' version of the 2-FUN software will be defined: it will use the calculation engine of Ecolego® for running simulations, performing probability analysis and sensitivity analysis, but a simple interface for end-users (e.g. regulators, consultants, etc) will be created (user interface optimized for making assessments using pre-defined models).

A similar approach will also be undertaken for the other sub-systems covered by the 2-FUN project, i.e. the 'soil/groundwater', 'out atmosphere/indoor air', 'plant', 'animal' and 'human' sub-systems.

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