2-FUN

***F**ull-chain and **UN**certainty Approaches for Assessing Health Risks in **FU**ture E**N**vironmental Scenarios*

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REVIEW OF FEATURES, EVENTS AND PROCESSES INCORPORATED IN EXISTING MULTI-MEDIA MODELS FOR SOILS AND GROUNDWATER

PROPOSAL OF THE CONCEPTUAL AND MATHEMATICAL 2-FUN MODEL FOR ASSESSING TRANSFER OF CONTAMINANTS IN SOILS AND GROUNDWATER

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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 soils[1].
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 soils is also described in detail.

[1] Reports related to freshwaters, palnts and animals was already published and reports will be published on other sub-systems of the environment (outdoor atmosphere, 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 sub-divided 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' systems;
- 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 soil and groundwater subsystems.

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 period 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).

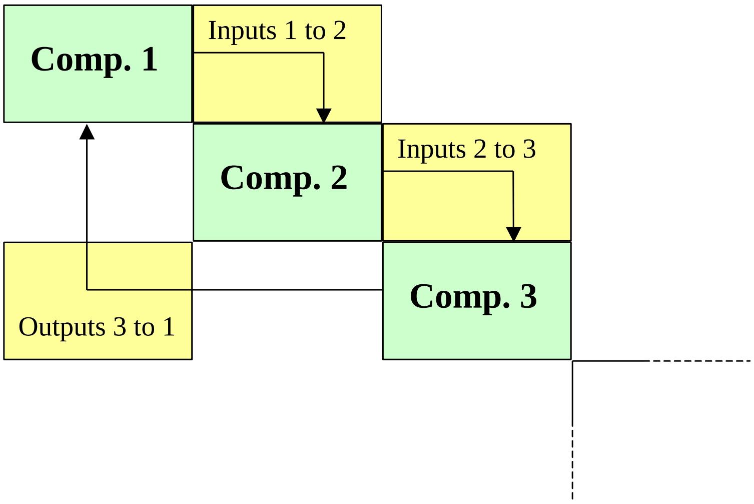

Figure 1 – The Interaction Matrix presentation

The Interaction Matrix will support the further mathematical implementation of the conceptual model[2]: 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 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.

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

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

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.

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
CemoS (similar to SAMS (OECD))	Mass balance steady-state box model included in the CemoS package	DTU (Dk)	Trapp and Matthies, 1998
CALTOX	Spreadsheet mass balance steady-state box model. The exposure model encompasses 23 exposure routes.	California EPA	Anonymous, 1993
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
PEARL	Dynamic multimedia model dedicated to pesticides	ALTERRA/RIVM (NL)	Leister et al, 2001
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 terrestrial ecosystems. The output concentrations from TRIM.FaTE can also be used as inputs to a human ingestion model.	US-EPA	US-EPA, 2002
XtraFood	Chain model for the analysis of contaminant in primary food products	VITO	Seuntjens, 2006

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.

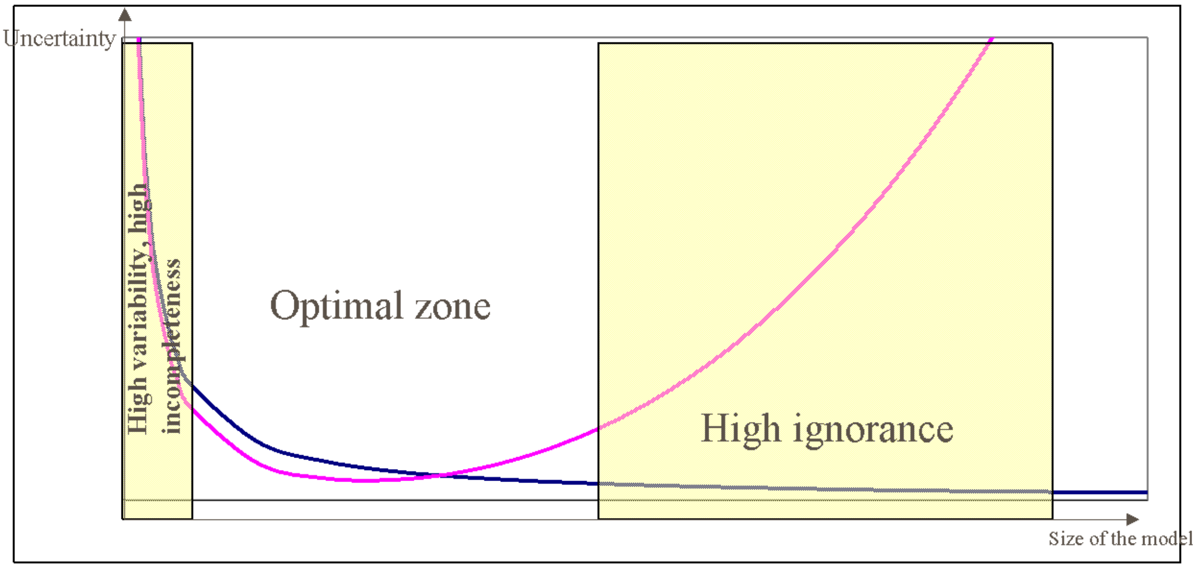

Figure 2 – Evolution of the uncertainty of the conceptual model and of data according to the complexity of the environment representation

The review undertaken in the frame of the 2-FUN project allowed identification of 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.

2.1 Interaction matrix of investigated models

Models which were analysed for the soil/groundwater system are listed in §1.5. Their respective Interaction matrices are represented in Figures 3-9[3].

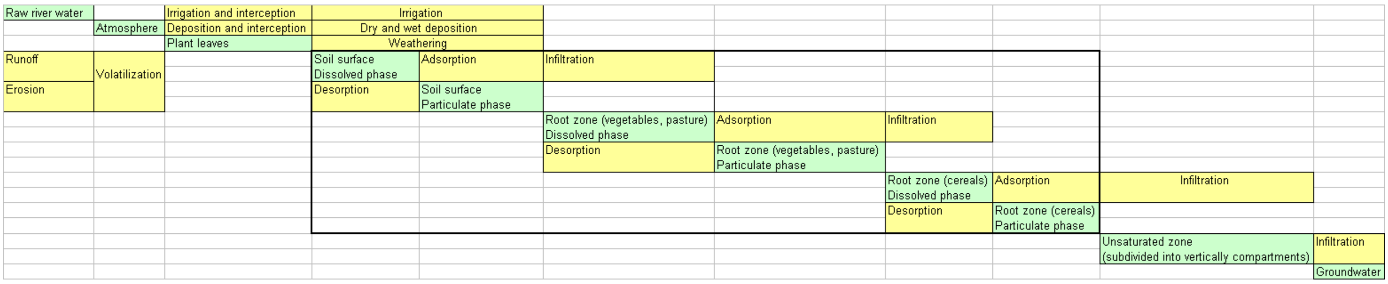

Figure 3– The OURSON Interaction Matrix for the soil sub-system

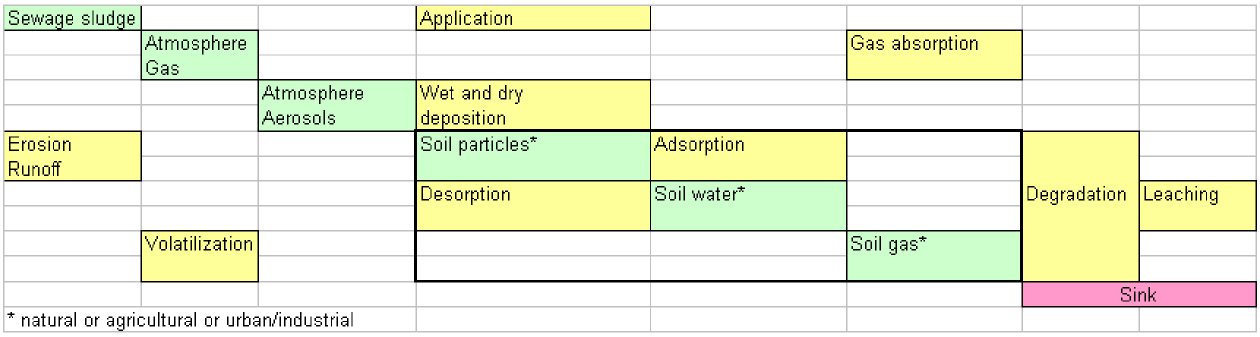

Figure 4 – The SimpleBox Interaction Matrix for the soil sub-system

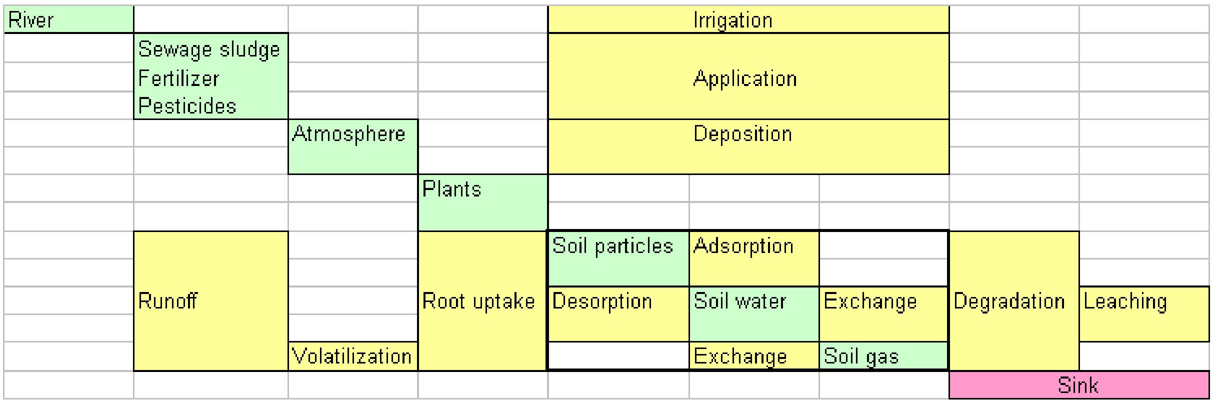

Figure 5 – The XtraFood Interaction Matrix for the soil sub-system

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

Raw river water							
	Atmosphere Vapor phase		Diffusion				
		Atmosphere Aerosols	Wet and dry deposition				
Soil solution runoff Erosion	Diffusion	Particles resuspension	Ground-surface soil	Downwards diffusion Advection			
			Upwards diffusion	Root-zone soil	Leaching		Degradation
					Vadose zone	Infiltration	
						Groundwater	
							Sink

Figure 6 – The CalTox Interaction Matrix for the soil sub-system

Agricultural chemicals			Application	Runoff	Application				
	Wastes				Sewage sludge appilacation - Deposits				
		Atmosphere	Deposition		Particle and gaseous deposition				
			Vegetation		Litter fall				
				Surface waters	Irrigation				
					Soil particles	Equilibrated partition			
					Equilibrated partition	Soil water	Equilibrated partition	Advection Dispersion	Degradation
		Volatilization				Equilibrated partition	Soil gas	Diffusion	
						Capillary transport		Groundwater	
									Sink

Figure 7 - The Cemos Interaction Matrix for the soil sub-system

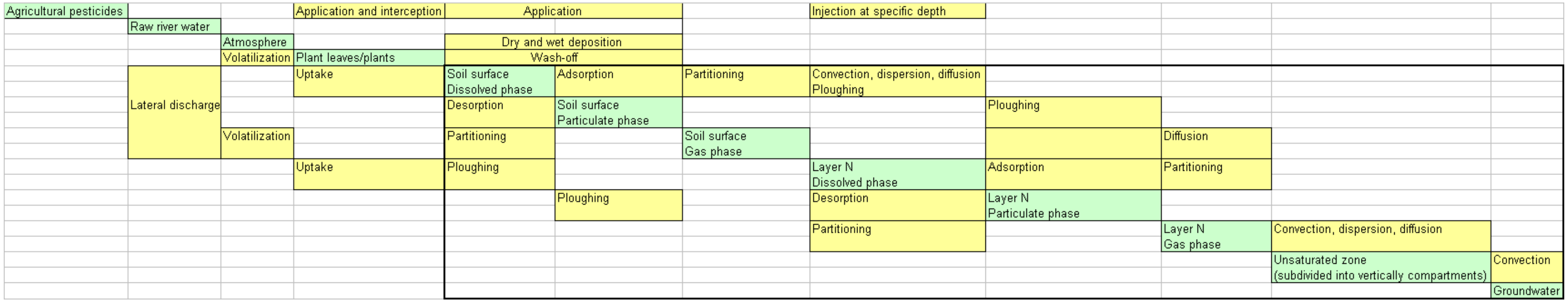

Figure 8– The PEARL Interaction Matrix for the soil sub-system

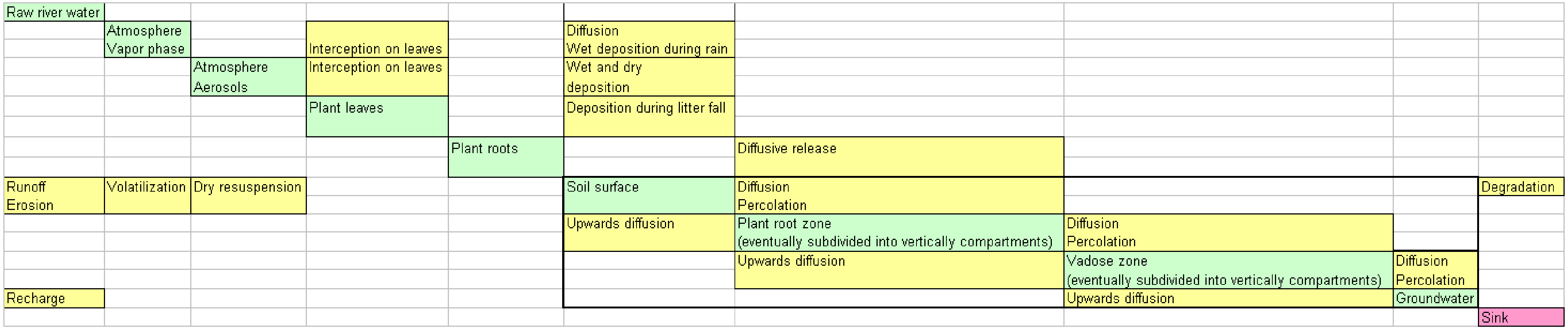

Figure 9 – The TRIM-FaTE Interaction Matrix for the soil sub-system

2.2 The compartments of the soil system

2.2.1 Depth profile in soils

Soil is by nature a continuous depth-dependent system. Two main options are possible to represent the depth-dependent pollution in soils:

- Many models (e.g. OURSON, Caltox, TrimFate, BUCKET module in Cemos, PEARL) consider that soil can be sub-divided in several layers, each of them being assumed to be homogeneous (i.e. in OURSON or Caltox, pollutants are homogeneously 'diluted' in a given soil layer) or exponentially distributed (i.e. in TrimFate, pollutant concentration exponentially decreases in each layer). The number and depth of the soil layers is crucial because they define the volumes in which pollutants are diluted, and they are thus sensitive parameters for the calculation of the contaminant redistribution in soil. At least four layers are generally defined in such models:
  - ✓ The soil surface layer (called also 'ground-surface soil' in CalTox). This compartment is theoretically defined as those directly interacting with the atmosphere (e.g. through volatilization) or surface waters (through runoff and/or erosion). A major issue is to select a relevant depth for this compartment (i.e. what is the actual soil depth interacting with atmosphere and rivers?). For example, CalTox states that 'studies of radioactive fallout […] reveal that […] particles deposited from the atmosphere accumulate in and are resuspended from a thin ground- or surface-soil layer with a thickness in the range 0.1 to 1 cm'. Ciffroy et al (2006) reviewed values used in several radioecological models and proposed the same range. Nevertheless, varying the depth of soil surface by one order of magnitude significantly modifies the 'dilution volume' in which pollutant deposited on soils are mixed. Besides, the range proposed above, based on the mean depth penetration of particles, was not verified for gaseous exchanges (diffusion at the soil/atmosphere interface) and for runoff/erosion processes and becomes then an 'arbitrary' value for such processes.
  - ✓ The root zone. The root zone is the layer interacting with plant through root uptake. Its definition is thus based on the root penetration of the plants of concern, and not on the actual behaviour and profile of contaminants in the soil. For poorly mobile compounds (i.e. substances interacting with soil particles), and for plants showing 'high' root penetration depths (like e.g. cereals, maize, fruit trees), the assumption of concentration be homogeneous in the whole layer may be irrelevant. The root zone can thus be subdivided in different sub-layers.
  - ✓ The vadose zone (also called unsaturated zone) is the intermediate layer separating root zone and groundwater. It may be eventually subdivided into several sub-compartments, the concentration in each of them being established by a mass balance equation.
  - ✓ Groundwater is generally considered as a homogeneous 'dilution' box and no model considers transport of contaminants within groundwater (e.g. to a pumping point).
- Some models (e.g. SimpleBox, XtraFood) consider that soil is an unique compartment in which contaminants are homogeneously diluted. These models can thus be considered similar to the ones previously described, but without soil surface layer and no description of the transport to groundwater. Problems already identified for the description of exchanges with atmosphere and surface waters are then also valid here. It must however be noted that, in SimpleBox, soil depth is substance-dependent: a penetration depth depending on the intrinsic properties of the compound (in particular, partition coefficient with soil particles) is defined and thus, soil depth does not systematically correspond to the actual rooting zone. For agricultural soils submitted to ploughing, a minimum depth is defined (20 cm). The penetration depth is the depth at which, at steady state, the rate of degradation is equal to the

rate of diffusive movement (i.e. calculated from the $(D_E/k)^{1/2}$ ratio, where k is the first order degradation rate and D_E the 'diffusion/advection' coefficient).

- Some models (e.g. recent update of SimpleBox (Hollander et al, 2004, 2007), Cemos) considers the soil as an unique layer, but a depth profile is calculated according an analytical relationship. For example, Hollander et al (2007) assumed that contaminant profile in soil is exponentially distributed (i.e.

$$c(z) = c_0 . \exp(-\frac{z}{d_p}),$$

where c(z) and c_0 are the concentrations at depth z and at the surface, and d_p is a penetration depth depending on advection velocity and dispersion coefficient) and they implemented this relationship in a recent version of SimpleBox. Cemos proposes three analytical solutions allowing the calculation of pollutant concentration in function of depth and time; these three solutions correspond to the following assumptions regarding inputs: (i) pulse input; (ii) contaminated layer (i.e. source within a soil layer); (iii) continuous injection.

In conclusion, several options are possible to represent the redistribution of contaminants in soils:

- the subdivision of soil into several layers (e.g. surface, root zone, vadose zone, groundwater, each of them being eventually subdivided) which are assumed to be homogeneous (i.e. the substance of concern is homogeneously distributed within a given layer);
- an unique homogeneous soil compartment, but with a pollutant-dependent depth;
- an unique soil compartment for which a depth-dependent profile is calculated from analytical solution of the 1D general transport equation in soils[4] .

Question 2.a: **What to choose among the three options for representing the redistribution of chemicals in soils (several homogeneous layers, or one layer with a pollutant-dependent depth, or one unique soil compartment with a depth-dependent profile calculated from analytical solutions)?**

It must also be noted that some models (CalTox, Cemos, TrimFate) take into account potential upwards movement of water by capillarity and/or diffusion. Upwards capillarity movement may indeed occur when evapo-transpiration from soil surface exceeds rainfall and thus when water content in upper soil layers is close to wilting point.

Question 2.b: **Is it necessary to represent upwards capillarity for calculating the redistribution of contaminants in soils?**

2.2.2 Groundwater

In all the models which consider groundwater (OURSON, Cemos CalTox, TrimFate), this compartment is considered to be homogeneous and pollutants are instantaneously diluted in its total volume. As for the unsaturated zone, a depth profile (and even a 3D profile for point sources) should be considered to calculate a more realistic concentration at a, e.g., pumping point.

Question 2.c: **is it necessary to simulate a spatial distribution (e.g. depth profile) of contaminants in groundwater?**

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[4] $$\frac{\partial c}{\partial t} = -v_e . \frac{\partial c}{\partial z} + D_e . \frac{\partial^2 c}{\partial z^2} - kc$$

2.3 The inputs/outputs into/from the soil system

2.3.1 Direct inputs

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

- Direct dry and wet depositions of contaminants present in the atmospheric aerosols are considered in all the models. 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, TRIM.FaTE, CemoS) also consider transfer of atmospheric gaseous pollutants to soil, but approaches for simulating it differ:
  - ✓ In SimpleBox, the overall mass transfer coefficient for atmospheric gas absorption, and inversely for volatilization of contaminants present in the soil, is estimated by a two-film resistance model at the air-soil interface, resulting from the summation of resistances at the air and soil sides respectively; the soil-side of the interface is treated as a pair of parallel resistance, corresponding to the air and water phases of the soil respectively. In Caltox, only the air phase of the soil-side (and not the dissolved phase) is taken into account for calculating mass transfer. 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 the PEARL model, only the boundary air layer through which the pesticide has to diffuse before escaping into the atmosphere is considered (i.e. only one resistance instead of two for SimpleBox). Diffusion rates of chemicals require the determination of boundary layer thicknesses and of diffusivities;
  - ✓ 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. Wet deposition of vapour gas requires then the definition of a vapour-phase scavenging ratio (i.e. the ratio between the contamination in rainwater and in gas respectively), assumed to be the inverse of the air/water partition coefficient (g chemical/m^3 air per g chemical/m^3 water).

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

- Some models (OURSON, CemoS) include irrigation (and associated pollutants in river or groundwater) as a potential input to soils. This process is however more or less detailed among the models under review. The most detailed representation of irrigation was found in OURSON: irrigation rates are calculated from water budget in soils; irrigation occurs only when a water deficit is calculated (i.e. when water content is close to wilting point) and is fitted to allow water recharge in soils (i.e. to reach field capacity). Irrigation is then meteorological-dependent.

Question 2.e: **is it necessary to include time-dependency (i.e. meteorological-dependency) in the calculation of irrigation rates?**

- Several models take also into account direct application of sludge, fertilizers, etc on soils. PEARL distinguishes different supply practices of pesticides to the soil: (i) at specified application times to the soil surface; (ii) at specified application times incorporated into the soil over a specified depth; (iii) at specified application times injected in soil at a specified depth (injection of fumigants).

2.3.2 Indirect inputs

Some models (e.g. SimpleBox, Caltox) consider that contaminants falling from the atmosphere under dry and wet deposits (as well as irrigation inputs) integrally and directly reach soil; the interception of a fraction of these contaminants by plants is then not taken into account in the mass balance model for soil surface. Instead, other models (e.g. OURSON, Cemos, TrimFate, PEARL) explicitly consider that a fraction of deposits is intercepted by leaves and does not contaminate soil surface immediately. However, the simulation of interception processes, as well as of delayed leaves-to-soil transfer, differ among models:

- ✓ In TrimFate, the fraction of dry deposits that is intercepted by plants is assumed to be constant. Instead, the fraction of wet deposits that is intercepted by plants is calculated according to the Leaf Area Index (i.e. m^2[total leaf area]/m^2[underlying soil area], a 'vegetation-dependant leaf-wetting factor' (i.e. a retention factor, in m) and amount of rainfall during a rainfall event;
- ✓ In OURSON, both the intercepted fractions of dry and wet deposits respectively are calculated taking into account an Interception coefficient (similar to the TrimFate's 'leaf-wetting factor') and the aerial biomass (or Leaf Area Index). Aerial biomass is however a time-dependent variable because it is assumed to increase until harvest;
- ✓ The intercepted fraction of contaminants can however reach soil with a retardation time through: (i) litter fall (indicated in Cemos and TrimFate as potential processes, but not appearing explicitly in the set of equations), and/or (ii) continuous transfer from leaves to soil by climate processes (wind, rain, etc), called 'Wash-off' in TrimFate and PEARL, and 'Weathering' in OURSON. In OURSON and TrimFate, this 'weathering' process is simulated through a constant weathering (or wash-off) loss rate, expressed in day^{-1}. In TrimFate, the loss rate is calculated to ensure that the particle mass on the leaves does not change (i.e. as much wet-deposited as is washed off).

Question 2.f: **is it necessary to take into account the interception by leaves to derive the mass balance model for soil?**
Question 2.g: **if interception by leaves is considered, is it necessary to simulate the time-dependency of this process? Besides, is it necessary to simulate transfer from leaves to soil (wash-off/weathering)?**

2.3.3 Losses

Several losses processes may be considered in modelling contaminant dynamics in soils.

- In almost all the models, losses from soil by erosion (of particles) and/or runoff (of dissolved contaminants) are considered. However, the approaches for modelling this pathway highly differ:
  - ✓ In SimpleBox, 'Soil to surface water' transfer by runoff and erosion is 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' and 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. However it must also be underlined that, in the mass balance model for a 'soil region', it is necessary to incorporate losses by runoff/erosion, but also inputs from adjacent regions submitted to runoff/erosion. It would thus be necessary to determine the 'directions' of runoff/erosion (in other words, the parameter called in

TrimFate 'fraction of water that runs off of surface soil compartment *i* that is transported to compartment *j*). This 'dimensional' requirement of the model is often difficult to be realistically satisfied;

- ✓ In OURSON, the input is simulated by a time-dependent transfer function assuming that deposition fluxes from the atmosphere are continuously eliminated from the soil. Two first-order loss rate constants are defined (i.e. loss of a pulse input can be represented by two exponential terms), representing rapid and slow runoff respectively. These loss rate constants were calibrated from measurements collected after pulse events (e.g. Chernobyl accident or bombs deposits);
- ✓ In PRZM and PEARL (models dedicated to pesticides), losses by runoff is simulated according the empirical SCS curve number method (USDA, 1986): volume of soil water submitted to runoff is assumed to be empirically related to the intensity of each rainfall event (with no runoff for rainfall below a given limit intensity) and to a Curve Number parameter depending on landscape characteristics (e.g. soil type, plant canopy, slope). This method requires nevertheless a precise knowledge on the number and intensity of each rainfall events, because, if (e.g. monthly) averaged rainfall are entered in the model, null runoff would be calculated. This method can thus be envisioned only if site-specific daily precipitations are available.

Question 2.h: **what is the best approach to include runoff/erosion processes (constant rain water reaching surface water, exponential transfer function, SCS curve number approach, mechanistic model requiring site-specific geographical characteristics)?**

- As indicated previously, only TrimFate simulates the exchange of chemicals between groundwater and surface waters. The approach chosen for simulating such groundwater storage and recovery processes is nevertheless simple: a transfer factor (in day^{-1}) is defined for representing global transfer from groundwater to surface waters; it depends on the groundwater volume, the fraction of pollutant under dissolved form and a macroscopic parameter called 'recharge' (annual average daily recharge from groundwater into surface water, in m.day^{-1}).

Question 2.i: **is it necessary to include in the model exchanges at the groundwater/river interface ? If yes, is the TrimFate approach sufficiently reliable?**

- Transformation processes in soils 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). The different transformation processes (hydrolysis, photolysis, microbial degradation) are generally not explicitly distinguished, but added into an aggregated loss rate.

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

2.4 The inter-compartment transfers within the soil system

Several phase transfer are considered between components belonging to the soil system:

- Exchanges of contaminants between the pore water and particles in soil. In all the models (except PEARL), 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 porewater respectively. For neutral 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;

- Exchanges of contaminants between pore water and gas contained in soil. Because soil surface is unsaturated, it may contain a fraction of gas. A fraction of pollutants can be associated to the soil vapour phase. In all the models, the partition between pore water and gas is described by the the adimensional Henry's law constant (representing the ration between vapour pressure and solubility of the chemical, corrected by temperature).

3. THE SOIL/GROUNDWATER 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 Calculation of the depth profile in soils

This section intends to provide elements for answering to the question 2.a: **What to choose among the three options for representing the redistribution of chemicals in soils (several homogeneous layers, or one layer with a pollutant-dependent depth, or one unique soil compartment with a depth-dependent profile calculated from analytical solutions)?**

Most of the multimedia models considered that soil can be represented by a succession of homogeneous boxes, the transfer between these latter being governed by advection and diffusion. Several limitations can be identified for this approach:

- 'Soil surface' is assumed to be the compartment in direct interaction with the atmosphere, i.e. dry and wet deposits are assumed to be homogeneously distributed in this layer, but also all the pollutants present in 'soil surface' are assumed to participate to diffusion processes at the soil/atmosphere interface. The depth of the 'soil surface' compartment was actually defined according to penetration depth of particles, as stated in Caltox ('studies of radioactive fallout [...] reveal that [...] particles deposited from the atmosphere accumulate in and are resuspended from a thin ground- or surface-soil layer with a thickness in the range 0.1 to 1 cm'). The relevance of such depth values for diffusive processes was scarcely discussed and remain questionable;
- Usually, the number of compartments into which the soil is divided is chosen arbitrarily and generally for 'practical' aspects. Instead, it was demonstrated that a compartmental model can provide valid results only if the minimum number of compartments is set to a specific value determined by the advection/diffusion flow conditions. For example, Kirchner (1998) calculated the minimal number of compartments to be included for a proper description of soil, in different flow conditions; as an example, for convection-dominated flow,

  $$N = \frac{v_w . L}{2D},$$

  where N is the number of compartments, v_w the pore water advection velocity, L the total soil depth and D the diffusion coefficient. Similar relationships can be found in other compartmental models described in Basagaoglu et al (2002), Bidwell (1999) or Sardin et al (1991).

In conclusion, the description of soil as a succession of successive soil layers would require: (i) a reliable definition of the layer actually in interaction with the atmosphere; (ii) a flexible definition of the number of compartments according to the depth of the unsaturated zone and to hydraulic parameters (advection flow velocity and diffusion coefficient).

The second option which was proposed in multimedia models (in SimpleBox) was to define a substance-dependent depth for an unique soil compartment, calculated according the chemical characteristics of the pollutant of concern. This approach can be considered as 'soil-oriented' because it actually (and theoretically) defines the layer which can be assumed to be homogeneous (instead of choosing it arbitrarily); it is however not 'plant-oriented' because it does not make reference to the actual rooting zone of each plant to be simulated further in the integrated approach.

The third option is to calculate the time-dependent and depth-dependent concentration of the pollutant in soil C(z,t) from the 1D general transport equation in soils:

(1) $$R.\frac{\partial C}{\partial t} = -v_e.\frac{\partial C}{\partial z} + D_e.\frac{\partial^2 C}{\partial z^2} - kC,$$

where:

- C(z,t): concentration of the pollutant at time t and depth z ($mg.m^{-3}$);
- R: retardation factor (-);
- v_e: pore water advection velocity ($m.d^{-1}$);
- D_e: diffusion/dispersion coefficient ($m^2.d^{-1}$) ;
- k : first-order rate constant for contaminants degradation (day^{-1}).

Corrected diffusion/dispersion coefficient $D_e^* = \frac{D_e}{R}$, pore water advection velocity $v_e^* = \frac{v_e}{R}$ and first-order rate constant for contaminants degradation $k^* = \frac{k}{R}$ can be defined.

The retardation factor incorporates the adsorption of contaminants on the particulate soil phase and is included in the equation because only the dissolved phase is assumed to move along the depth profile (Kirchner, 1998; Toso and Velasco, 2001; Cokca, 2003) :

(2) $$R = 1 + \frac{\rho_{soil}.K_d}{\theta_{soil}},$$

where:

- θ_{soil} : water content in the soil (m^3 water.m^{-3} soil);
- ρ_{soil} : bulk mass density of the soil ($kg.m^{-3}$);
- K_d : distribution coefficient (i.e. ratio between particulate and porewater contamination respectively) ($m^3.kg^{-1}$).

Several analytical solutions were proposed in the literature, assuming uniform soil properties (water content and porosity), constant diffusion/dispersion coefficient D_e and flow velocity v_e, and various boundary conditions. For example:

- McKone and Bennett (2003) and Hollander et al (2006) assumed steady-state conditions and a fixed concentration boundary condition (i.e. constant concentration at z=0). Under such assumptions, they established that the vertical soil profile can be described by the following equation:

  (3) $$C(z) = C_0.\exp\left(-\frac{z}{d_p}\right), \text{ with } d_p = \frac{v_e^* + \sqrt{v_e^{*2} + 4k^* D_e^*}}{2k^*}.$$

  A more complex solution can also be demonstrated, which avoids some approximations of the previous one:

(4) $$C(z,t) == \frac{C_0.}{2}.\exp\left(\frac{v_e^* z}{2D_e^*}\right).\left\{\exp(-z\beta).\mathrm{erfc}\frac{z - t\sqrt{v_e^{*2} + 4k^* D_e^*}}{\sqrt{4D_e^* t}} + \exp(z\beta).\mathrm{erfc}\frac{z + t\sqrt{v_e^{*2} + 4k^* D_e^*}}{\sqrt{4D_e^* t}}\right\}$$

with $\beta = \sqrt{\frac{v_e^{*2}}{4D_e^2} + \frac{k^*}{D_e^*}}$

and erfc is the complementary error function.

....

- it is also possible to derive an analytical solution for a pulse input (Dirac input m_0 ($kg.m^{-2}$) at time t_0=0 and z_0=0), as described in e.g. Trapp and Matthies (1998) and Cokca (2003):

(5) $$C(z,t) = \frac{m_0}{\sqrt{4\pi D_e^* t}}.\exp\left(-\frac{(z - v_e^* t)^2}{4D_e^* t}\right).\exp(-k^* t)$$

- Trapp and Matthies (1998) proposed also a solution when a contaminated soil layer is the initial condition (i.e. C(z=h, t=0)=C_0, anywhere else C(t=0)=0).

Taking into account this background, a method must be selected and justified for the further implementation in the 2-FUN model. The specifications for the 2-FUN model can be summarized as follows:

- to select a method able to simulate dynamic inputs onto soil surface (i.e. time-dependent inputs);
- to select a method able to provide an estimation of the mean concentration in the rooting zone of each plant further incorporated in the full-chain assessment framework.

Equation (3) would be the easiest one to implement, but suffers from some limitations. It is limited to steady-state conditions (even if partly tested for unsteady conditions by Hollander et al (1998)) and, as stated by Hollander et al (2007), it should be limited to compounds strongly interacting with soil particles, i.e. to substances with $\log(K_{ow}) > 3$. Equation (4) is also limited to steady-state conditions (and then fixed boundary condition at z=0).

An other option enabling to use analytical solutions of the 1D general transport equation could be to consider the continuous time-dependent input as a succession of pulse inputs and to assume a superposition principle (i.e. each pulse input behaves independently in the soil profile). Assuming such an approximation (additive independent contributions $m_{T-t,}$ at date T-t), the soil profile can be obtained as follows:

(6) $$C(z,T) = \int_{t=0}^{T} \frac{m_{T-t}}{\sqrt{4\pi D_e^*(T-t)}} \exp\left[-\frac{(z - v_e^*(T-t))^2}{4D_e^*(T-t)}\right] \exp(-k^*(T-t))\, dt$$

where:
m_{T-t} : deposit at time T-t ($mg.m^{-2}.s^{-1}$).

However, the superposition principle is questionable because diffusion of a pulse input can't be reliably simulated without taking into account the historic background contamination of the soil.

For the 2-FUN approach, it was then proposed to subdivide the root zone in N layers and to discretize the 1D general transport equation, i.e.

(7) $$\frac{\partial C}{\partial t} = -\frac{v_e}{R}.\frac{\partial C}{\partial z} + \frac{D_e}{R}.\frac{\partial^2 C}{\partial z^2} - \frac{k}{R}.C\,,$$

with R defined by Equation (2).

According to the Method of Lines for partial differential equations, Equation (7) can be written for each soil layer i as follows:

(8) $$\frac{\Delta C_i}{\Delta t} = -\frac{v_e}{R}.\frac{C_i - C_{i-1}}{\Delta z} + \frac{D_e}{R}.\frac{C_{i+1} - 2.C_i + C_{i-1}}{\Delta z^2} - \frac{k}{R}.C_i$$

Since Equation (7) is first order in t and second order in z, it requires one auxiliary condition in t and two auxiliary conditions in z. t is termed an initial value variable and therefore requires one initial condition $C(z,t_0)$. z is termed a boundary value variable and therefore requires two boundary conditions $C(z=0,t)=f_0(t)$ and $C(z=\infty,t)=f_\infty(t)$.

As previously indicated, the main problem of this approach is to define a reliable number of compartments N to be included for a proper description of soil. As this number N depends on both advection and diffusion coefficient (and then on scenario conditions), it must be flexible and chosen as a variable by the end-user.

3.2 Capillarity processes

This section intends to provide elements for answering question 2.b : **is it necessary to represent upwards capillarity for calculating the redistribution of contaminants in soils?**

Capillarity rise of water (and associated pollutants) is a process depending on several environmental factors, especially: (i) the evaporation demand of the atmosphere; (ii) the water extraction pattern of roots, governing a potential deficit of water in the topsoil layer; (iii) the water content in the topsoil as a result of rainfall and eventually irrigation; (iv) the depth of groundwater below the soil surface; (v) the thickness and characteristics of successive layers in the soil profile (if it is not relevant to consider that it is homogeneous).

Although the mechanistic representation of these processes is complex, several water flux models were developed, based on Richards equation (e.g. SWAP model) or transient analytical equations. However, these deterministic approaches require the description of soil hydraulic properties, which limit their use because of the lack of data and the difficulty to obtain them.

Several empirical and semi-empirical approaches were also proposed to evaluate the groundwater contribution to topsoil moisture through capillarity rise. These approaches aim at determining the upward and downward fluxes of water in the vadose zone as the result of capillarity rise and infiltration respectively. The most popular approach is originated from Doorenbos and Pruitt (1977) and allows the calculation of upward and downward fluxes through the root zone boundary. Thus, the upward water flux (called also groundwater contribution), expressed in $mm.day^{-1}$, is given by:

(9) $$v_u = \begin{cases} v_{u,max} & \text{if } W < W_{wp} \\ v_{u,max}.\left(\dfrac{W_p - W}{W_p - W_{wp}}\right) & \text{if } W_{wp} \le W < W_p \\ 0 & \text{if } W_p \le W < W_{fc} \end{cases}$$

The downward water flux (called also deep percolation), expressed in $mm.day^{-1}$, is given by:

(10) $$v_d = \begin{cases} 0 & \text{if } W < W_{fc} \\ W - W_{fc} & \text{if } W > W_{fc} \end{cases}$$

where:

- W: actual soil water storage in the root soil (mm);
- W_{fc}: soil water storage at field capacity in the root zone (mm);
- W_{wp}: soil water storage at wilting point in the root zone (mm);
- W_p: soil water storage corresponding to the depletion fraction for no stress (mm);
- $v_{u,max}$: potential groundwater contribution (mm.day^{-1}).

These equations were built according to the following assumptions:

- the water storage in the root zone can be subdivided into different fractions: (i) the excess water fraction, corresponding to gravitational water and corresponding to the fraction exceeding water content at field capacity; (ii) the 'optimal yield' fraction, where water is readily available by plants to reach maximal yields, and corresponding to water content between W_p and W_{fc}; (iii) the water stress fraction, where water is low enough to induce plant stress, and corresponding to water content between W_{wp} and W_p;
- downward water flux occurs only for excess water, i.e. for the fraction exceeding field capacity;
- upward water flux is null when optimal conditions required by plants are satisfied; if these optimal conditions are not satisfied, upward flux depends on actual water storage in the root zone and the state of stress.

Because upward water flux modifies the water storage in topsoil, it may have an indirect effect on drainage, and thus on vertical movement of pollutants leaving the root zone to the vadose zone.

The approach chosen in multimedia models which explicitly take into account upward movement in soils (CalTox, Cemos, TrimFate) is simpler: upwards capillarity movement occurs indeed when evapotranspiration from soil surface exceeds rainfall. The underlying assumptions are thus that: (i) water budget in topsoil is influenced only by instantaneous difference between precipitation and evapotranspiration, while it should include other inputs and losses (e.g. irrigation, drainage, groundwater contribution); (ii) water budget in topsoil is not influenced by water demand by plants.

This approach can be improved in the 2-FUN model according to the following assumptions:

- upward and downward water fluxes, corresponding to capillarity rise from groundwater and drainage respectively, can be calculated according to equations (10) and (11);
- the actual soil water storage in the root soil W can be iteratively computed by taking into account all the inputs and loss processes in topsoil, i.e.

  (11) $$\frac{dW}{dt} = P_e + Irr + G_c - ET_a - D_r$$

  where:

  - ✓ P_e: effective precipitation (mm.d^{-1});
  - ✓ Irr: daily irrigation rate (mm.d^{-1});
  - ✓ G_c: groundwater contribution to water storage (mm.d^{-1});
  - ✓ ET_a: actual evapotranpiration (mm.d^{-1});
  - ✓ D_r: deep percolation loss (drainage) (mm.d^{-1}).

- the actual evapotranspiration $ET_a(t)$ may be estimated by taking into account the potential evapotranspiration $ET_p(t)$ and a time-dependent cultural coefficient $K_c(t)$ that may be lower or higher to unity according to the stage of development of the plant. The actual evapotranspiration $ET_a(t)$ at time t (mm.month^{-1}) is thus calculated as follows (according to the FAO model (Doorenbos and Pruitt (1977), cited in Maraux et al, 1998):

(12) if $W_p < W < W_{fc}$, then $ET_a(t) = K_c(t).ET_p(t)$

(13) if $W_{wp} < W < W_p$, then $ET_a = \frac{W(t)}{W_p} K_c(t).ET_p(t)$

At a monthly time scale, potential evapotranspiration $ET_p(t)$ can be given by the Turc's relationship:

(14) $$ET_p(t) = 0.4 \frac{T(t)}{T(t)+15}(Ig(t)+50)$$

where:

- ✓ $ET_p(t)$: potential evapotranspiration at time t ($mm.month^{-1}$);
- ✓ $T(t)$: mean atmospheric temperature at time t (°C);
- ✓ $Ig(t)$: global solar radiation at time t ($cal.cm^{-2}.j^{-1}$).

- the vertical movement of pore water in soils can be considered as the net result of downward infiltration (drainage) minus upward capillarity rise. The pore water advection velocity v_e, used in Equation (1) to calculate the vertical redistribution of pollutants in soils can thus be calculated as:

(15) $$v_e(t) = v_d(t) - v_u(t)$$

3.3 Spatial distribution of contaminants in groundwater

This section intends to provide elements for answering to the question 2.c : **is it necessary to simulate a spatial distribution (e.g. depth profile) of contaminants in groundwater?**

As previously indicated (see 2.2.2), all the models consider that pollutants entering into groundwater from the unsaturated zone are immediately and homogeneously diluted in the global volume of the 'groundwater box'. If a well is situated below the water table, it would however be useful to evaluate the depth profile of pollutants in groundwater.

As a simplified assumption (acceptable because of the high dispersion in the unsaturated zone), it may be considered that input of pollutants into groundwater is at steady-state. In such conditions, the general transport model in groundwater (similar to those in soil described in Equation (1)), can be solved as (according to similar assumptions as those described for Equation (3)) :

(16) $$C_{groundwater}(z) = C_{0\_groundwater}.\exp\left(-\frac{z}{d_p}\right), \text{ with } d_p = \frac{v_e^* + \sqrt{v_e^{*2} + 4k^* D_e^*}}{2k^*}.$$

where:

- $C_{groundwater}(z)$: concentration of the pollutant at depth z below the water table (z=0) ($mg.m^{-3}$);
- R: retardation factor (-);
- $v_e^* = \frac{v_e}{R}$: pore water advection velocity corrected by the retardation factor R ($m.d^{-1}$);
- $D_e^* = \frac{D_e}{R}$: diffusion/dispersion coefficient corrected by the retardation factor R ($m^2.d^{-1}$) ;

- $k^* = \frac{k}{R}$: first-order rate constant for contaminants degradation corrected by the retardation factor R (day^{-1}).

The retardation factor incorporates the adsorption of contaminants on the particulate soil phase and is included in the equation because only the dissolved phase is assumed to move along the depth profile:

(17) $$R = \frac{1}{\varepsilon_{groundwater} + \rho_{groundwater}.K_{d,groundwater}},$$

where:

- $\varepsilon_{groundwater}$: water content (or porosity) in groundwater (m^3 water.m^{-3} soil);
- $\rho_{groundwater}$: bulk mass density of groundwater ($kg.m^{-3}$);
- $K_{d\_groundwater}$: distribution coefficient (i.e. ratio between particulate and porewater contamination respectively) in groundwater ($m^3.kg^{-1}$).

3.4 The air-soil interactions

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

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

- 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 soils, i.e. dry and wet deposition of aerosols, gaseous wet deposition following rain dissolution, and absorption/volatilization at the atmosphere/soil interface.

3.5 Irrigation rates

This section intends to provide elements for answering to the question 2.e : **is it necessary to include time-dependency (i.e. meteorological-dependency) in the calculation of irrigation rates?**

As previously indicated (see 2.3.1), most of the models adopt a simple simulation for representing irrigation process: it is indeed assumed that irrigation is permanent and independent of the meteorological conditions, soil moisture and/or plant water stress. Such assumptions are obviously not realistic because irrigation rates are generally governed by local meteorological conditions and yield expectations.

However, because water availability is limited in some regions, models were developed for irrigation scheduling (e.g. George et al, 2000; Liu et al, 1998; Chopart et al, 2007). Quantitative irrigation scheduling are based on monitoring (crop water stress monitoring or soil moisture monitoring) or on water balance modeling approaches. Modeling approaches are generally based on water budgeting over the root zone, including all the processes influencing water content in soil (rainfall, evapotranspiration, drainage, groundwater contribution).

In the 2-FUN model, it is proposed to follow the FAO's methodology (Doorenbos and Pruitt (1977), Maraux et al, 1998) already described in paragraph 3.2 to calculate water budget in soil (see equations 12 to 15)

In can be decided that irrigation occurs only when actual water storage in soil induces a water stress for plants (i.e. $W<W_p$). Different irrigation scheduling options are possible:

- fixed interval (e.g. irrigation occurring once a week, etc);
- fixed depth (i.e. X mm for each irrigation event, independently of stress intensity);
- 'management allowable depletion', including variable interval and variable depth.

In the 2-FUN model, it is proposed to simulate the 'fixed depth' option (realistic assumptions for many agricultural behaviors). In such a case, the model can be summarized as:

If $W(t)<W_p$, then $Irr(t)=Irr_{fixed\_depth}$,

where Irr_{fixed_depth} is a fixed depth irrigation rate (in mm).

3.6 Interception of pollutants by leaves and weathering from leaves to soil

This section intends to provide elements for answering to the questions 2.f and 2.g: **is it necessary to take into account the interception by leaves to derive the mass balance model for soil?** and **if interception by leaves is considered, is it necessary to simulate the time-dependency of this process ? Besides, is it necessary to simulate transfer from leaves to soil (wash-off/weathering)?**

Plants may take up chemical through several pathways: (i) root uptake; (ii) gas diffusion at the leaf-atmospheric gas interface; (iii) deposition onto leaves of atmospheric contaminated particles; (iv) interception onto leaves of rain contaminated by scavenged chemicals. In many models, no reliable description of the last two processes (i.e. interception of atmospheric particles and rain) is proposed (it is even ignored in some models). Such processes influence the contamination of plants (especially plant leaves), but they also govern the quantity of chemicals reaching (directly or indirectly) soil (chemicals intercepted by leaves being not directly deposited to soil).

However, some experimental observations showed that the fraction of atmospheric contaminants intercepted by leaves is not negligible and should be taken into account in the mass budget calculations. For example, several experiments were conducted with radionuclides as tracers of atmospheric aerosols (e.g. Pinder et al, 1988a; Pinder and McLeod, 1988b; Hoffman et al, 1992; Hoffman et al, 1995; Pröhl and Hoffman, 1996; Vandecasteele et al, 2002) and showed that, under some conditions (e.g. high Leaf area Index), the main part of atmospheric particulate contamination is intercepted by leaves. Some examples of intercepted fractions of particles and/or radionuclides (i.e. the ratio between the quantity retained by the vegetation and the total deposited quantity) are provided in Table 2 and demonstrate that, under some conditions, a large fraction of deposited pollutants do not reach directly soil, but are intercepted by leaves. For organic pollutants, the relative importance of intercepted particles versus gaseous diffusion obviously depends of the partitioning in the atmosphere between aerosols and gas phase (described by the octanol-air partion coefficient K_{OA}). For some pollutants mainly associated to atmospheric particles (e.g. PAHs), the interception of particulate dry or wet deposits can play a predominant role (Smith and Jones, 2000; Barber et al, 2004). It is then justified to include this process in the modelling of the soil contamination (especially in case of time-dependent dynamic models).

Wet vs dry deposition	Deposited material	Particle diameter (µm)	Crop	Intercepted fraction (%)	Reference
Dry deposition	^{85}Sr, ^{133}Ba, ^{137}Cs	3.5	Beans	84	Madoz-Escande et al, 2004
Dry deposition	Silica particles	4 10 18 22 4 22	Lettuce Wheat	71 88 88 81 56 65	Watterson and Nicholson, 1996
Wet deposition	Mixture of radionuclides		Rice Soybean Cabbage Radish	from 48 to 94% from 34 to 93% from 16 to 87% from 18 to 86%	Choi et al, 2002
Wet deposition	^{137}Cs		Wheat Beans Grass	from 1.4 to 7.4% from 1 to 5.9% from 1.1 to 3.6%	Kinnersley et al, 1997

Table 2 – Some experimental values of intercepted fractions of radionuclides or particles

Several mechanistic models were proposed to simulate the interception of particles and/or wet deposits onto leaves and to take into account the leaves 'morphology'. A 'popular' formulation is those proposed by Chamberlain (1970), which stated:

(18) $$f_{intercepted} = 1 - \exp(-\alpha_{interception}.B_{aerial})$$

where:

- $f_{intercepted}$: interception fraction (-) (i.e. ratio of the intercepted quantity and the total deposited quantity);
- $\alpha_{interception}$: interception coefficient (-);
- B_{aerial}: above-ground biomass (kg DW.m^{-2} soil).

This relationship reflects the fact that the interception fraction increases as the plant grows (and the surface of leaves increases). It was for example implemented in the urban multimedia model developed by Diamond et al (2004) (only for dry deposits).

The Chamberlain's model was experimentally supported for pasture grass and other leafy crops, but, for cereals, Pröhl and Hoffmann (1996) proposed a more appropriate normalization by Leaf Area Index LAI (in m^2 leaves.m^{-2} soil):

(19) $$f_{intercepted} = 1 - \exp(-\alpha^*_{interception}.LAI)$$

Similarly, for wet deposits, Müller and Pröhl (1993) proposed a relationship accounting for the LAI and the rainfall intensity (used in the urban multimedia model developed by Diamond et al (2004)):

(20) $$f_{wet\_intercepted} = \frac{LAI.S}{R}\left[1 - \exp(-\frac{\ln 2}{3.S}.R)\right]$$

where:

- S: retention coefficient (-);
- R: amount of rainfall (mm).

The term $\left[-\frac{\ln 2}{3.S}\right]$ is based on the assumption that 50% of the maximum storage capacity of the leaf is reached for a rainfall amounting to three times that of this storage capacity. However, when this equation is applied, $f_{wet\_intercepted}$ can be greater than unity for low rainfall, which is unrealistic.

The models presented in equations (19) to (21) propose a macroscopic description of the interception process. Some more complex models tried to subdivide the interception global process into different consecutive and/or competitive sub-processes governing the interactions of pollutants with plant leaves (Petroff et al, 2008), i.e. (i) Brownian diffusion, affecting very fine particles and representing the deposition through the boundary layer surrounding the leaves; (ii) 'interception', for particles following the streamline of the flow field and interacting with the leaves according to their diameter; (iii) impaction, representing the collision of a particle against an obstacle; (iv) sedimentation, representing the gravity movement of particles; (v) rebound. Petroff et al (2008) proposes an integrated model combining each of these processes. However, it clearly appears that such a complex mechanistic model is out of the scope of the 2-FUN multimedia model because too difficult to parameterize.

For the 2-FUN multimedia model, it is then proposed to simulate the interception of dry and wet deposits onto leaves by the Chamberlain's relationship (equation 19) (or the Pröhl's one (equation 20), if enough experimental data can be found during the parameterization process for establishing PDFs).

Once the pollutants are intercepted onto plants, they can be washed off from leaves to soils; loss of contamination from the foliar surface has several origins, such as wind removal, water removal and dilution by plant growth. All the losses can simply be represented by a global loss constant for foliar surface λ_w. For example, Miller and Hoffman (1983) reviewed 78 values determined under various experimental conditions and for several contaminants presenting contrasted level of mobility, allowing the parameterization of such a macroscopic model.

3.7 Transfer from soil to surface waters

This section intends to provide elements for answering to the question 2.h: **what is the best approach to include runoff/erosion processes (constant rain water reaching surface water, exponential transfer function, SCS curve number approach, mechanistic model requiring site-specific geographical characteristics) ?**

Pollutant 'wash-off' designates the transport of contaminants in water flowing over the soil surface and finally reaching freshwater systems (rivers and/or lakes). It includes runoff of dissolved contaminants and erosion of contaminated soil particles. Wash-off from watersheds is a loss process from soils and can be a significant secondary input into freshwaters because these latter collect water and particle fluxes from potentially wide areas, especially during rainfall.

The choice of a model for simulating wash-off highly depends on the spatial and temporal scales covered by the multimedia model, as well as on the availability of data for the calibration and site-specific applications. Wash-off is indeed by nature intermittent as it is related to the rainfall regime: it increases after heavy rainfalls, floods and snowmelt. Besides, it can show high spatial variability, even at small scales, because it depends on the slope of the field and on its cover. Two quite different approaches were proposed so far to incorporate runoff in multimedia models:

- 'freshwater-oriented' approaches. Their objective is to estimate the input into surface waters of pollutants deposited onto watersheds and washed-off. These approaches are generally based on global transfer functions directly relating atmospheric deposits onto soils and inputs into rivers. For example, the SimpleBox multimedia model assumed that a constant proportion of rainwater directly reaches freshwater systems 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). Thus, SimpleBox directly connects rainwater to freshwater through a constant transfer rate and shunts many processes actually occurring in natural soil systems. More recently, time-dependent (instead of permanent) transfer functions were developed, especially in the field of radioecology. Such models were calibrated using datasets collected after the Chernobyl accident for a wide range of European rivers; the Chernobyl accident corresponds indeed to a 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, 2008);
- 'soil-oriented' approaches. Some mechanistic or empirical models take into account short kinetic and spatial variations in the rainfall regime to simulate the loss of runoff water from soil during a given meteorological event. For example, the PRZM multimedia model incorporated the 'SCS runoff curve number approach' developed by USGS (USDA, 1986). This approach calculates the soil depth impacted by runoff according to the rainfall event and to an empirical parameter (called 'curve number') implicitly accounting for landscape characteristics (like hydrologic soil group, slope of the field and land use coverage). This approach was however developed exclusively from a terrestrial point of view: it intends to predict the loss of water, particles and eventually associated contaminants from the soil rather than to calculate the global input of pollutants in freshwaters running across the watershed.

In the integrated 2-FUN multimedia model, it is necessary to propose a 'freshwater- and soil-oriented' approach which could simulate homogeneously both the loss of pollutants from soils and their flux into rivers.

It is then proposed to use the model previously implemented in the 'Freshwater' module of the 2-FUN model (see 2-FUN's Deliverable 2.1). This model directly defines a flux of pollutants running from soil to freshwaters and thus a half life of pollutants in the soil system; the wash-off flow rate of the pollutant at time t ($\Phi_{wash-off}(t)$) from soil into the freshwater system is calculated as follows:

(21) $$\Phi_{wash-off}(t) = D_{soil}(t_0).S_{watershed}.\lambda_{wash-off}(t)$$

where:

- ✓ $\Phi_{wash-off}(t)$ (mg.d^{-1}): wash-off flow rate entering into the freshwater system at time t;
- ✓ $D_{soil}(t_0)$ (mg.m^{-2}): deposit flux on the soil surface at time t_0=0;
- ✓ $S_{watershed}$ (m^{-2}): surface of the watershed influencing the region under investigation;
- ✓ $\lambda_{wash-off}(t)$ (d^{-1}): wash off rate constant at time t after the pulse deposit.

3.8 Recharge from groundwater to surface waters

This section intends to provide elements for answering to the question 2.i: **is it necessary to include in the model exchanges at the groundwater/river interface ? If yes, is the TrimFate approach sufficiently reliable?**

In many catchments, groundwater and surface water are hydraulically connected. These interactions (e.g. surface waters receiving groundwater from underlying aquifers) may have implications in the transfer of pollutants along the chain soil-vadose zone-groundwater-surface waters.

Different configurations can be found:

- connected streams, when the stream (fully or partially) penetrates the aquifer (see Figure 10). When a stream fully penetrates an unconfined aquifer there are two cases to be considered. In the first case, called a connected gaining stream, the groundwater table is higher than the water level in the stream and water flows from the aquifer to the stream. In the second case, called a connected losing stream, the water table is below the stream water level and water flows from the stream into the aquifer;

- disconnected streams, when the stream does not (fully or partially) penetrates the aquifer (see Figure 11). In this case, according to the position of the water table from the stream, the flow from this latter can be affected or not.

The 2-FUN model described below proposes a simulation approach only for connected gaining streams.

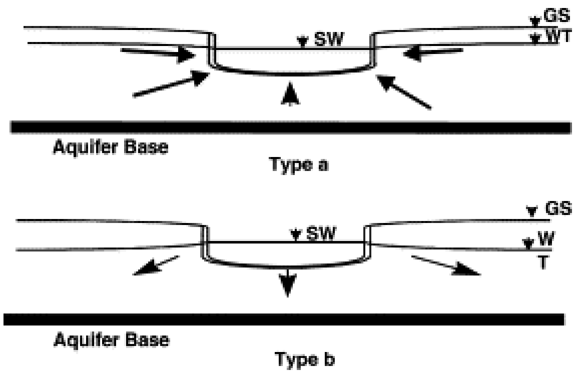


Figure 10 - Interaction aquifer-river with hydraulic connection. c : connected gaining stream. d : connected losing stream (from Osman et Bruen, 2002)

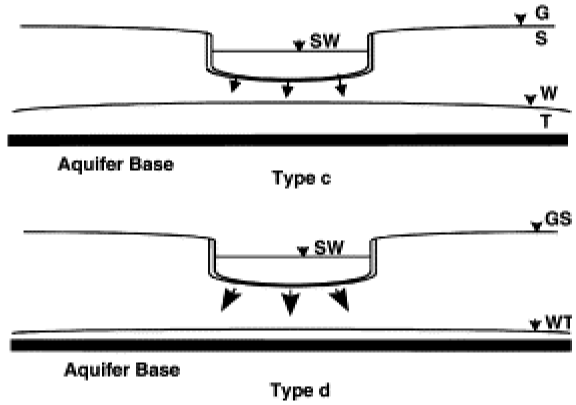


Figure 11- Interaction aquifer-river without hydraulic connection. c :superficial water table. d : deep water table (from Osman et Bruen, 2002)

Complex models (e.g. MODFLOW, MODCOU) were proposed to simulate the water exchanges between aquifer and surface waters. However, such approaches generally require a spatial representation of water table and streams, as well as the knowledge on several parameters (streambed saturated hydraulic conductivity, thickness of the streambed, elevation of the water surface of the stream and aquifer head). In many cases, the limited number of existing data collection points results in a lack of information limiting a relevant calibration

Alternative approaches were proposed for empirically calibrating exchange rates between groundwater and surface waters (only in the case of connected gaining streams). Such approaches were based on the analysis of hydrographs: a hydrograph is the time-series record of water flow of the investigated river. For a gaining stream, where groundwater is contributing to the stream flow, analysis of the hydrograph can indicate the magnitude and timing of this contribution.

An observed hydrograph (i.e. flow rate in function of time) can be separated into two components:

- the baseflow, i.e. the flow resulting from natural storage, mostly assumed to be originated from unconfined aquifer;
- the quickflow, corresponding to the direct response to a rainfall, including runoff (overland flow), interflow (lateral movement in the soil profile) and direct input onto the stream surface.

The analysis of hydrograph during rainfall events (especially flood or storm events) allows to estimate the time-dependency of the baseflow (assumed to be the input from groundwater and surface waters) (see Figure 12

) :

1. during the prior low-flow conditions, the stream is assumed to be originated from the baseflow at the end of a dry period;
2. at the beginning of rainfall, the stream is dominated by quickflow (runoff and interflow). The rapid increase in the stream level relative to surrounding groundwater leads to a reduction of the baseflow;
3. during the third stage, the quickflow component decreases, leading to a declining stream level. Because of the delayed response of a rising water table from infiltrating rainfall, the hydraulic gradient towards the stream increases, leading to an increase of the base flow.

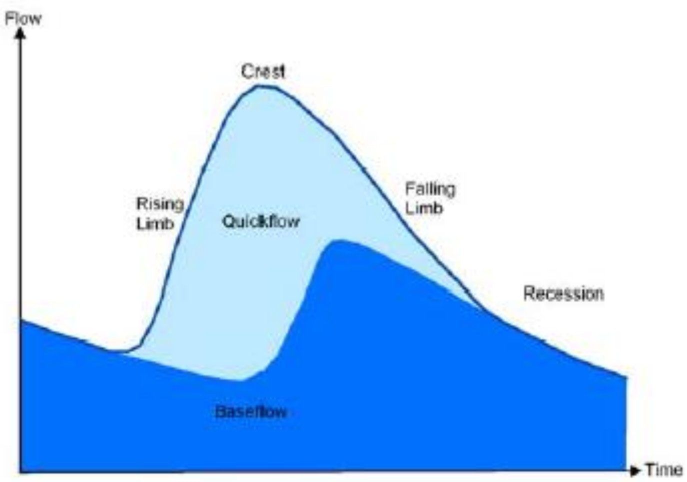


Figure 12 – Components of a typical flood hydrograph (from Brodie et al, 2007)

Several methods were proposed to separate the different components of the hydrograph and thus to estimate the time-dependent flow from groundwater to surface waters:

- Graphical separation methods or Filtering separation methods. Such methods can produce several index which can be of interest for multimedia modeling, such as the mean annual baseflow volume and the long-term average daily baseflow. These methods are based on an iterative analysis of the baseflow and the total flow of the stream. As an example, the filter method proposed by Chapman et al (1996) is based on the following equation: $q_{b(i)} = \frac{k}{2-k} q_{b(i)} + \frac{1-k}{2-k} q_{(i)}$, where $q_{b(i)}$ is the baseflow at the date i, $q_{(i)}$ is the total flow rate at the date i, k is the filter parameter. Other filters were proposed in the literature (e.g. Furey and Gupta, 2001).

- Recession analysis. This method focuses the analysis on the specific part of the flood hydrograph after the crest, where streamflow decreases (see 'falling limb and recession' parts in Figure 11). The recession period lasts until streamflow begins to increase again because of a rainfall. Recession analysis is based on a selection of recession segments, which can be interpreted individually or collectively. Traditionally, a linear storage-outflow model based on the classical exponential decay function was used, according to the following equation:

(22) $$Q_t = Q_0 . e^{-\frac{t}{T_c}} ,$$

where

- ✓ Q_t : stream flow at time t ;
- ✓ Q_0 : stream flow at the start of the recession segment;
- ✓ T_c : residence time or turnover time of the groundwater system defined as the ratio of storage to flow.

This approach allows thus to estimate an average residence time of water in the aquifer and could be adapted for its incorporation in a multimedia model, because it can be parameterized by using readily available datasets. In particular, it could be a physical foundation for the parameterization of the model proposed in TRIM.FaTE, which is based on a 'recharge rate' (annual average daily recharge from groundwater into surface water, in $m.day^{-1}$).

It must also be noted that alternative models were proposed, allowing to address non-linearity in recession (e.g. Cheng, 2008) or to represent aquifer as multiple reservoirs with different residence times.

One of the major limitations of this approach is however that it can be used only for connected gaining streams.

- Frequency analysis methods. Frequency analysis is based on flow duration curves (FDC), describing the percentage of time that a given flow rate is equaled or exceeded (Smakhtin, 2001). Such FDCs can be built from daily, weekly or monthly flow rates for example. The slope of the FDC can be interpreted for collecting information about baseflow (see Figure 13). Baseflow is considered to be significant for low-flow conditions (right part of the curve), if the curve has a low slope, as this reflects continuous discharge to the stream. A high slope in this part of the curve can indicate losing streams. Frequency analysis methods allow thus to discriminate between gaining and losing streams and to verify that recession analysis, which is valid only for gaining streams, can be used for representing aquifer-stream connectivity.

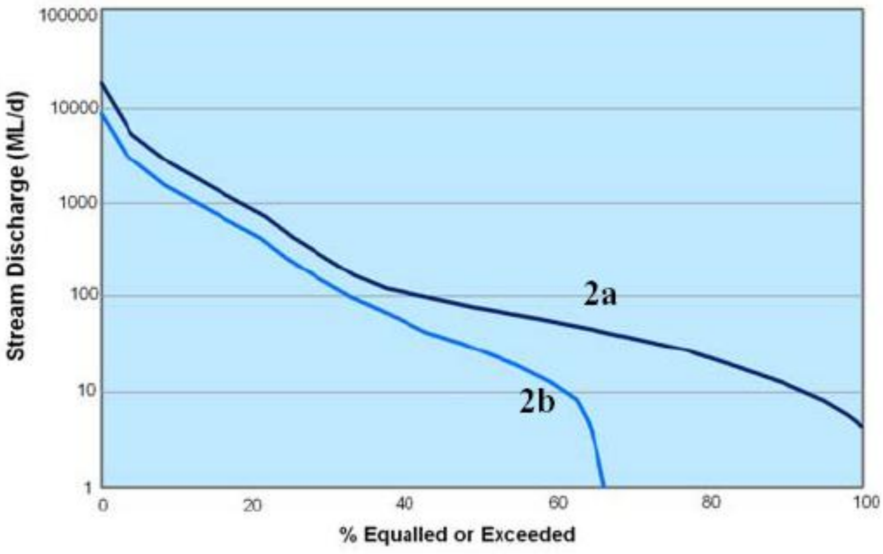


Figure 13 – Examples of Flow distribution curves - (2a) high baseflow – (2b) low baseflow streams

In conclusion, it can be envisioned to implement a simple method for simulating the recharge from groundwater to surface waters and the associated transport of contaminants dissolved in groundwater. This approach is based on the definition of a mean residence time of groundwater and associated dissolved contaminants in the aquifer; contaminants lost from the aquifer are integrally transferred to the adjacent surface stream. It can be suggested to use recession analysis methods (which use readily available datasets on flow rates) to determine the averaged residence time T_c.

In this context, the kinetic evolution of pollutant concentration in the aquifer can be described by the following equation:

(23) $$\frac{dC_{aquifer}}{dt} = -\frac{1}{T_c}.C_{aquifer,dis} = -\frac{1}{T_c}.\frac{1}{\varepsilon + \rho_{aquifer}.K_d}C_{aquifer}$$

where

- ✓ $C_{aquifer}$: concentration of the pollutant in the aquifer ($g.m^{-3}$);
- ✓ $C_{aquifer,dis}$: concentration of the pollutant dissolved in the aquifer ($g.m^{-3}$);
- ✓ ε : porosity in the aquifer (-);
- ✓ $\rho_{aquifer}$: bulk mass density of the aquifer ($kg.m^{-3}$);
- ✓ K_d : distribution coefficient (i.e. ratio between particulate and porewater contamination respectively) ($m^3.kg^{-1}$).

3.9 Processes of transformation

This section intends to provide elements for answering to the question 2.j: **is it sufficient to use a 'global' degradation rate implicitly including several degradation processes?**

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.

3.10 The 2-FUN Interaction Matrix for the soil/groundwater system

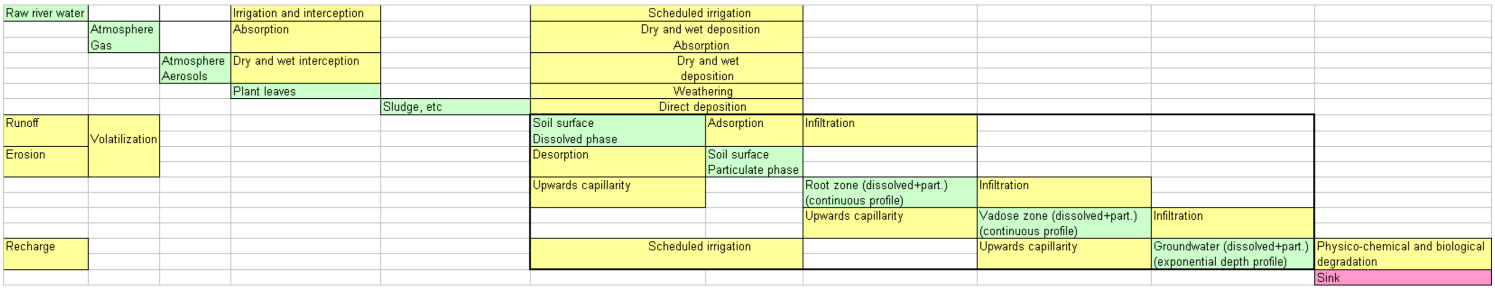
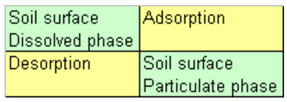


Figure 14- The 2-FUN Interaction Matrix for the soil/groundwater sub-system

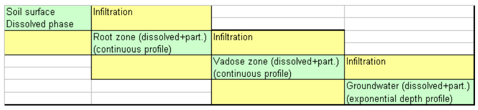
The 2-Fun Interaction matrix for soil/groundwater system (Figure 13) was built by taking into account the analysis previously detailed.

The main principles of this conceptual model are summarized below:

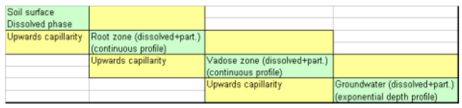
- Each soil depth zone (soil surface, root zone, vadose zone, groundwater) was subdivided in two sub-compartments (dissolved and particulate phases respectively). An equilibrium was assumed between these two phases through the use of a partition (or distribution) coefficient, governing a retardation factor.



- Convective transport is assumed to govern the transfer of contaminants downwards (in the direction surface-root zone-vadose zone-ground water). A retardation factor was introduced to take into account the distribution dissolved-particulate; the mean flow velocity is calculated by taking into account the water budget in soil.



- Upwards capillarity movement is indirectly taken into account because it is incorporated in the calculation of water budget in soil (and thus it leads to a decreasing of the downwards flow velocity).

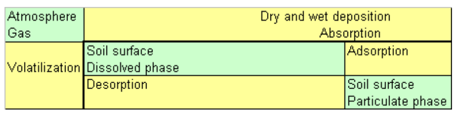


- Dry deposition of pollutants associated to aerosols was simulated through a constant deposition velocity of the aerosols particles.

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

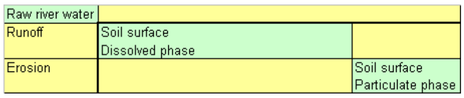
- Dry deposition of vapour-phase pollutants was simulated through a constant deposition velocity calculated through an analogy to electrical resistance.

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

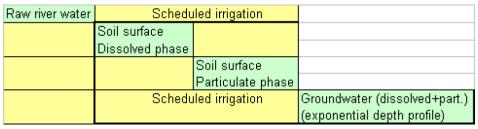


Absorption/volatilization of semi-volatile substances at the air-freshwater interface was modelled using the stagnant boundary theory (two-film model), the pollutant being assumed to diffuse across two layers (stagnant water layer and stagnant air layer) characterized by two resistances in series.

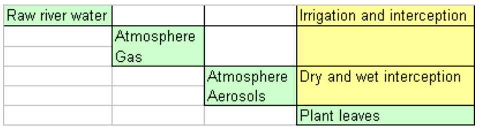
- Outputs by erosion-runoff of contaminated soils was taken into account through the use of a kinetic transfer function measuring the flux from soils to surface waters (and using a half life rate constant).



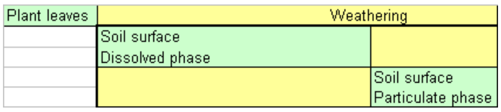
- Irrigation occurs only when actual water storage in soil induces a water stress for plants. The ‘fixed depth’ irrigation scheduling option is proposed.



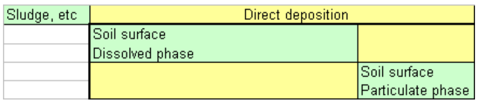
- Interception of contaminants by plant leaves (following dry and/or wet deposition) is taken into account as it decreases the flux directly reaching soil surface.



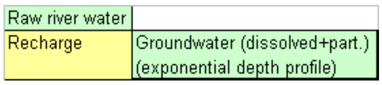
- Transfer from plant leaves to soil (dry and wet contamination) by weathering (wind and rain actions) is taken into account through a half life of contaminants onto leaves.



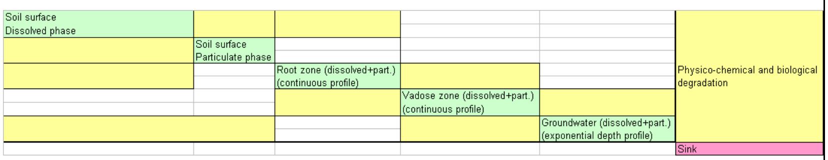
- Direct deposition of contaminated sludge is taken into account.



- Transfer of contaminants from groundwater to surface waters is taken into account through a mean residence time of contaminants in groundwater.



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



4. THE SOIL/GROUNDWATER 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 soil/groundwater subcompartment (i.e. soil surface, root zone, interface vadose zone/groundwater) was derived from inputs/outputs/transformation processes previously selected and mathematically described in the present section, according to a mass-balance system.

It must be noted that several soil sub-locations (or sub-regions) can be considered in the model, e.g. 'bare soil' locations, locations where vegetables are cultivated, locations where pasture is cultivated, locations where cereals are cultivated, etc. The number of sub-regions will be defined in agreement with the plant model (Deliverable 2.4). In this document, only the contamination of a generic region (e.g. generic soil surface C_{soil_surf}) will be described, but, in the actual model, the equations will be implemented for different regions (e.g. $C_{soil\_surf,bare\_soil}$, $C_{soil\_surf,cereals}$, etc).

4.1 Preliminary calculations: water dynamics in soil

For calculating the dynamics of pollutants in soils, it is previously necessary to calibrate some parameters describing the dynamics of water flows in the soil system, i.e. the mean groundwater contribution (v_u in Equation (10)), the mean percolation flux (v_d in Equation (11)), the daily irrigation rate. Water storage in soil is described by three main parameters, governing the movement of water in the system, i.e.

- W_{fc}: soil water storage at field capacity in the root zone (mm);
- W_{wp}: soil water storage at wilting point in the root zone (mm);
- W_p: soil water storage corresponding to the depletion fraction for no stress (mm),

with $W_{wp} < W_p < W_{fc}$.

The first stage of the calculation is the estimation of all the inputs/outputs of water to/from the root soil system, i.e. losses by evapotranspiration, inputs by irrigation, outputs by percolation and groundwater contribution.

4.1.1 Potential and actual evapotranspiration $ET_p(t)$ and $ET_a(t)$

Potential evapotranspiration $ET_p(t)$ is given by the Turc's relationship (relevant at a monthly scale):

(24) $$ET_p(t) = 0.4 \frac{T(t)}{T(t)+15}(Ig(t)+50)$$

where:

- ✓ $ET_p(t)$: potential evapotranspiration at month n ($mm.month^{-1}$);
- ✓ T_n: mean atmospheric temperature at month n (°C);
- ✓ Ig_n: global solar radiation at month n ($cal.cm^{-2}.d^{-1}$).

T_n and Ig_n are meteorological input data.

The actual evapotranspiration $ET_a(t)$ (in $mm.month^{-1}$) is estimated by taking into account the potential evapotranspiration $ET_p(t)$ and a time-dependent cultural coefficient $K_c(t)$ (input time-dependant dataset):

(25) if $W_p < W(t)$, then $ET_a(t) = K_c(t).ET_p(t)$

(26) if $W_{wp} < W(t) < W_p$, then $ET_a(t) = \frac{W(t)}{W_p} K_c(t).ET_p(t)$

4.1.2 Irrigation rates

In can be decided that irrigation occurs only when actual water storage in soil induces a water stress for plants (i.e. $W<W_p$). Different irrigation scheduling options are possible:

- fixed interval (e.g. irrigation occurring once a week, etc);
- fixed depth (i.e. X mm for each irrigation event, independently of stress intensity);
- 'management allowable depletion', including variable interval and variable depth.

In the 2-FUN model, it is proposed to simulate the 'fixed depth' scheduling irrigation, i.e.:

(27) if $W(t)>W_p$, then $Irr(t)=0$,

(28) if $W(t)<W_p$, then $Irr(t)=Irr_{fixed\_depth}$,

where Irr_{fixed_depth} : fixed depth irrigation rate (in $mm.d^{-1}$).

4.1.3 Percolation water flux

The downward water flux (called also deep percolation), expressed in $mm.day^{-1}$, is given by:

(29) $$v_d(t) = \begin{cases} 0 & \text{if } W < W_{fc} \\ W(t) - W_{fc} & \text{if } W > W_{fc} \end{cases}$$

4.1.4 Groundwater contribution

The upward water flux (called also groundwater contribution), expressed in $mm.day^{-1}$, is given by:

(30) $$v_u(t) = \begin{cases} v_{u,max} & \text{if } W < W_{wp} \\ v_{u,max} \cdot \left(\frac{W_p - W(t)}{W_p - W_{wp}} \right) & \text{if } W_{wp} \le W < W_p \\ 0 & \text{if } W_p \le W < W_{fc} \end{cases}$$

where

- $v_{u,max}$: potential groundwater contribution ($mm.day^{-1}$).

4.1.5 Water budget in the root zone of the soil

The actual soil water storage in the root soil W(t) can be iteratively computed by taking into account all the inputs and loss processes in topsoil, i.e.

(31) $$\frac{dW}{dt} = P_e(t) + Irr(t) + v_u(t) - ET_a(t) - v_d(t)$$

where:

- ✓ P_e: effective precipitation ($mm.d^{-1}$);
- ✓ Irr: daily irrigation rate ($mm.d^{-1}$);
- ✓ v_u: groundwater contribution to water storage ($mm.d^{-1}$);

- ✓ ET_a: actual evapotranpiration ($mm.d^{-1}$);
- ✓ v_d: deep percolation loss ($mm.d^{-1}$).

Taking into account Equations (26) to (31), three zones in the soil water storage can be distinguished:

(32) if $W_{wp}<W(t)<W_p$, then

$$\frac{dW}{dt} = P_e(t) + Irr_{fixed\_depth} + v_{u,max} \cdot \left(\frac{W_p - W(t)}{W_p - W_{wp}} \right) - \frac{W(t)}{W_p} K_c(t).ET_p(t)$$

(33) if $W_p<W(t)<W_{fc}$, then

$$\frac{dW}{dt} = P_e(t) - K_c(t).ET_p(t)$$

(34) if $W(t)>W_{fc}$, then

$$\frac{dW}{dt} = P_e(t) - K_c(t).ET_p(t) - \left[W(t) - W_{fc}\right]$$

4.2 Inputs/outputs onto the soil surface system[5]

4.2.1 Inputs from contaminated sludge and/or direct application

Point-source discharges (contaminated sludge and/or direct application, e.g. of pesticides) (expressed in $mg.m^{-2}.d^{-1}$) occurring onto the investigated soil surface (i.e. the investigated box) are taken into account as:

(35) $$\frac{dC_{soil\_surf,direct-appl.}}{dt} = \Phi_{direct\_application}$$

where :

- ✓ $dC_{soil\_surf,direct-appl.}$ ($mg.m^{-2}$): concentration onto soil surface due to point-source direct discharges (e.g. sludge deposition, pesticides application, etc);
- ✓ $\Phi_{direct\_application}$ ($mg.m^{-2}.d^{-1}$): time-dependent flux of pollutant onto soil surface due to point-source direct discharges.

4.2.2 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:

(36) $$\frac{dC_{soil\_surf,dry\_dep}}{dt} = \left[1 - f_{dry\_intercepted}(t)\right].\bar{v}_{dry,atm}.C_{part,atm}(t).TSP_{atm}$$

where:

- ✓ $\frac{dC_{soil\_surf,dry\_dep}}{dt}$ ($mg.m^{-2}.d^{-1}$): kinetic variation in the concentration of soil surface due to dry deposition of atmospheric particles;

[5] The 'soil surface' is defined as the soil at depth z=0.

- ✓ $C_{part\_atm}(t)$ (mg.g^{-1}): time-dependent concentration of particulate pollutant in the atmosphere;
- ✓ TSP_{atm} (g.m^{-3}): total suspended particles (aerosols) in the atmosphere;
- ✓ $v_{dry,atm}$ (m.d^{-1}) : dry deposition velocity of particles;
- ✓ $f_{dry\_intercepted}(t)$ (-) : time-dependent dry interception fraction onto plant leaves (i.e. ratio of the intercepted quantity and the total deposited quantity).

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

(37) $$C_{part\_atm}(t) = \frac{K_{p,atm}.C_{atm}(t)}{1 + K_{p,atm}.TSP_{atm}}$$

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 atmosphere[6];

The time-dependent interception fraction onto plant leaves $f_{dry\_intercepted}(t)$ is described by the Chamberlain's relationship (as stated in paragraph 3.6):

(38) $$f_{dry\_intercepted}(t) = 1 - \exp(-\alpha_{dry\_interception}.B_{aerial}(t))$$

where:

- ✓ $\alpha_{dry\_interception}$: interception coefficient (-);
- ✓ $B_{aerial}(t)$ (kg DW.m^{-2} soil) : time-dependent above-ground biomass.

Equation (39) requires the determination of the time-dependence of the above-ground biomass $B_{aerial}(t)$. In the 2-FUN model, it will be considered that $B_{aerial}(t)$ linearly increases from germination date to harvest date, i.e.:

(39) $$\text{if } t \notin [t_{germ} - t_{har}], \text{ then } B_{aerial} = 0$$

(40) $$\text{if } t \in [t_{germ} - t_{har}], \text{ then } B_{aerial}(t) = B_{aerial,har}.\left(1 - \frac{t_{har} - t}{t_{har} - t_{germ}}\right)$$

where:

- ✓ t_{germ}: germination date (-);
- ✓ t_{har}: harvest date (-);
- ✓ $B_{aerial,har}$ (kg DW.m^{-2} soil) : above-ground biomass at harvest.

We thus obtain :

(41) $$\boxed{\frac{dC_{soil\_surf,dry\_dep}}{dt} = [1 - \exp(-\alpha_{dry\_interception}.B_{aerial}(t))].v_{dry,atm}.TSP_{atm}.\frac{K_{p,atm}.C_{atm}(t)}{1 + K_{p,atm}.TSP_{atm}}}$$

with $B_{aerial}(t)$ calculated according to Equations (27) and (28).

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

4.2.3 Inputs from wet deposition of gaseous pollutants and aerosols

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

(42) $$\frac{dC_{soil\_surf,wet\_dep,part}}{dt} = \Lambda_{part}.Rain(t).\left(1 - f_{wet\_intercepted}(t)\right).\overline{C}_{part,atm}.TSP_{atm}$$

and

(43) $$\frac{dC_{rw,wet\_dep,gas}}{dt} = \Lambda_{gas}.Rain(t).\left(1 - f_{wet\_intercepted}(t)\right).\overline{C}_{gas,atm}$$

where :

- ✓ $\frac{dC_{soil\_surf,wet\_dep,part}}{dt}$ ($mg.m^{-2}.d^{-1}$): kinetic variation in the concentration of soil surface due to wet deposition of particles;
- ✓ $\frac{dC_{soil\_surf,wet\_dep,gas}}{dt}$ ($mg.m^{-2}.d^{-1}$): kinetic variation in the concentration of soil surface due to wet deposition of gaseous pollutants (rain dissolution);
- ✓ $C_{part\_atm}(t)$ ($mg.g^{-1}$): time-dependent concentration of particulate pollutant in the atmosphere;
- ✓ $C_{gas\_atm}(t)$ ($mg.m^{-3}$): time-dependent concentration of gaseous pollutant in the atmosphere;
- ✓ Rain(t) ($m.d^{-1}$) : time-dependent rainfall ;
- ✓ Λ_{part} (-) : rainfall scavenging ratio for particles (i.e. ratio between the concentration in rainwater (in $mg.m^{-3}$ rainfall) and in the particles ($mg.m^{-3}$ air) respectively);
- ✓ Λ_{gas} (-) : rainfall scavenging ratio for gas (i.e. ratio between the concentration in rainwater (in $mg.m^{-3}$ rainfall) and in gas ($mg.m^{-3}$ air) respectively);
- ✓ TSP_{atm} ($g.m^{-3}$ air): total suspended particles (aerosols) in the atmosphere;
- ✓ $f_{wet\_intercepted}(t)$ (-) : time-dependent wet interception fraction onto plant leaves (i.e. ratio of the intercepted quantity and the total deposited quantity).

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:

(44) $$C_{gas\_atm}(t) = \frac{C_{atm}(t)}{1 + K_{p,atm}.TSP_{atm}}$$

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 atmosphere[7];
- ✓ TSP_{atm} ($g.m^{-3}$): total suspended particles (aerosols) in the atmosphere.

As for the dry interception process, the time-dependent wet interception fraction onto plant leaves $f_{wet\_intercepted}(t)$ is described by the Chamberlain's relationship (as stated in paragraph 3.6):

[7] 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).

(45) $f_{wet\_interception}(t) = 1 - \exp(-\alpha_{wet\_interception}.B_{aerial}(t))$

where:

- ✓ $\alpha_{wet\_interception}$: interception coefficient (-);
- ✓ $B_{aerial}(t)$ (kg DW.m^{-2} soil) : time-dependent above-ground biomass.

Time-dependency of $B_{aerial}(t)$ is given by Equations (27) and (28

The combination of equations (30**Erreur ! Source du renvoi introuvable.**) to (33**Erreur ! Source du renvoi introuvable.**) gives:

(46)
$$\frac{dC_{soil\_surf,wet\_dep,part}}{dt} = \Lambda_{part}.Rain(t).\left[\exp(-\alpha_{wet\_interception}.B_{aerial}(t))\right]\frac{K_{p,atm}.TSP_{atm}}{\left(1 + K_{p,atm}.TSP_{atm}\right)}C_{atm}(t)$$

and

(47)
$$\frac{dC_{soil\_surf,wet\_dep,gas}}{dt} = \Lambda_{gas}.Rain(t).\left[\exp(-\alpha_{dry\_interception}.B_{aerial}(t))\right]\frac{C_{atm}(t)}{\left(1 + K_{p,atm}.TSP_{atm}\right)}$$

4.1.4 Inputs/outputs from diffusion of gaseous atmospheric pollutants[8]

Absorption/volatilization of semi-volatile substances at the 'air-soil surface' 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 soil to the atmosphere is driven by the fugacity difference between air and surface soil:

(48)
$$F_{soil-atm}(t) = D_{soil-atm}\left(C_{gas\_atm}(t) - \frac{H.C_{soil\_1,dis}(t)}{RT}\right)$$

where:

- ✓ $F_{soil-atm}(t)$ (mg.m^{-2}.d^{-1}): time-dependent net flux of the pollutant at the soil-atmosphere interface;
- ✓ $D_{soil-atm}$ (m.d^{-1}): gas-phase overall mass transfer coefficient;
- ✓ $C_{gas\_atm}(t)$ (mg.m^{-3}): time-dependent concentration of gaseous pollutant in the atmosphere;
- ✓ $C_{soil\_1,dis}(t)$ (mg.m^{-3}): time-dependent concentration of the pollutant in dissolved phase of the soil surface layer;
- ✓ H (Pa.m^3.mol^{-1}): Henry's law constant;
- ✓ R (8.205 Pa.m^3.mol^{-1}.K^{-1}): universal gas constant;
- ✓ T(t) (K): time-dependent temperature at the air-soil interface.

The term $\frac{H.C_{riv,dis}(t)}{RT}$ in equation **Erreur ! Source du renvoi introuvable.**(48) represents the gaseous concentration of the substance in the soil surface layer, assumed to be in equilibrium with the dissolved concentration. This equilibrium is simulated by the adimensional Henry's law constant.

[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:

(49) $$\frac{1}{D_{soil-atm}} = \frac{1}{D_{soil-atm,g}} + \frac{H}{RT.D_{soil-atm,w}}$$

where:

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

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

(50) $$C_{soil\_1,dis}(t) = \frac{C_{soil\_1,tot}(t)}{K_{d,soil}}$$

where:

- ✓ $C_{soil\_1,tot}(t)$ (mg.m^{-3}): time-dependent total concentration of the pollutant in soil surface;
- ✓ $K_{d,soil}$ (m^3.g^{-1}): distribution coefficient of the pollutant at the interface water-soil particles.

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

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

(51) $$\boxed{K_{d\_soil} = 10^{-6} \cdot y_{OC,soil}.K_{OC}}$$

where :

- ✓ $y_{OC,SPM}$ (-) : massic organic fraction in soil;
- ✓ K_{OC} (-):octanol-organic carbon partition coefficient.

Moreover, the partition of pollutant in the atmosphere between aerosols and gas is described by a partition coefficient $K_{p,atm}$ (see equation (37**Erreur ! Source du renvoi introuvable.**)).

4.1.5 Outputs from erosion-runoff of contaminated soils

Erosion and runoff (gathered under the terminology ‘Wash-off’) of chemical substances at the ‘air-river interface was modeled using a constant wash-off rate constant:

(52) $$Wash\_off = \lambda_{wash\_off}.\Delta h_{layer\_1}.C_{soil\_1,tot}(t)$$

where:

- ✓ $Wash\_off$ (mg.m^{-2}.d^{-1}): time-dependent flux of pollutant from soil to the river;
- ✓ $\lambda_{wash\_off,i}$. (d^{-1}): wash-off rate constant;
- ✓ Δh_{layer1} (m): depth of the surfacic soil layer;
- ✓ $C_{soil\_1,tot}(t)$ (mg.m^{-3}): volumetric pollutant concentration of soil layer1 (soil surface).

4.1.6 Inputs from irrigation

The inputs of contaminants from the river to cultivated soils through irrigation can be modelled by considering the irrigation rate defined in Equations (27) and (28) :

(53) $$\frac{dC_{soil,surf,irr}}{dt} = 10^{-3}.Irr(t).C_{raw\_water}(t)$$

where:

- ✓ $\frac{dC_{soil,surf,irr}}{dt}$ (mg.m^{-2}.d^{-1}): time dependent output of pollutant from raw river water due to irrigation of cultivated soils;
- ✓ $C_{raw\_water}(t)$ (mg.m^{-3}): time dependent concentration in raw river water used for irrigation
- ✓ $Irr(t)$ (mm.d^{-1}): irrigation rate of cultivated soils.

4.1.7 Output from groundwater recharge

The outputs of contaminants from groundwater to the river through recharge (only for connected losing streams) can be modelled by considering the irrigation rate defined in Equations (27) and (28) :

(54) $$\frac{dC_{groundwater}}{dt} = \frac{1}{\varepsilon + \rho_{aquifer}.K_{d,aquifer}} \frac{C_{groundwater}(t)}{T_c}$$

where:

- ✓ $\frac{dC_{groundwater}}{dt}$ (mg.m^{-3}.d^{-1}): time dependent output of pollutant from groundwater due to recharge of the river;
- ✓ $C_{groundwater}(t)$ (mg.m^{-3}):
- ✓ ε (-): porosity of groundwater;
- ✓ $\rho_{aquifer}$ (kg.m^{-3}): bulk mass density of the aquifer;
- ✓ $K_{d,aquifer}$ (m^3.kg^{-1}): distribution coefficient in the aquifer (i.e. ratio between particulate and porewater contamination respectively);
- ✓ T_c (d): residence time or turnover time of the groundwater system defined as the ratio of storage to flow.

4.3 Transport of pollutants in soil

For the 2-FUN approach, the root zone is subdivided in N layers and to the 1D general transport equation is discretized, i.e.

(55) $$\frac{\partial C}{\partial t} = -\frac{v_e}{R}.\frac{\partial C}{\partial z} + \frac{D_e}{R}.\frac{\partial^2 C}{\partial z^2} - \frac{k}{R}.C\ ,$$

where:

- R(-): retardation factor;
- v_e ($m.d^{-1}$): pore water advection velocity;
- D_e ($m^2.d^{-1}$) : diffusion/dispersion coefficient;
- k (d^{-1}) : first-order rate constant for contaminants degradation.

R is defined as follows:

(56) $$R = 1 + \frac{h_{rz}.\rho_{soil}.K_{d,soil}}{10^{-3}.W(t)},$$

where:

- W(t) (mm): time dependent soil water storage in the root soil (mm);
- h_{rz}: (m): height of the root zone;
- ρ_{soil} : bulk mass density of the soil ($kg.m^{-3}$);
- $K_{d,soil}$: distribution coefficient (i.e. ratio between particulate and porewater contamination respectively) ($m^3.kg^{-1}$).

v_e is defined as follows:

(57) $$v_e = v_d - v_u$$

where :

- v_d ($mm.d^{-1}$): downward water flux (called also deep percolation) (see equation (29));
- v_u ($mm.d^{-1}$): upward water flux (called also groundwater contribution) (see equation (30)).

According to the Method of Lines for partial differential equations, Equation (55) can be written for each soil layer i as follows:

(58) $$\frac{\Delta C_i}{\Delta t} = -\frac{v_e}{R}.\frac{C_i - C_{i-1}}{\Delta z} + \frac{D_e}{R}.\frac{C_{i+1} - 2.C_i + C_{i-1}}{\Delta z^2} - \frac{k}{R}.C_i$$

As previously indicated, the main problem of this approach is to define a reliable number of compartments N to be included for a proper description of soil. As this number N depends on both advection and diffusion coefficient (and then on scenario conditions), it must be flexible and chosen as a variable by the end-user. However, it is necessary to check the following condition:

(59) $$N > \frac{v_e.h_{rz}}{2D_e}$$

For the transport in the unsaturated zone (below the root zone), the same equation is used; the height of the root zone (h_{rz}) is replaced by the height of the root zone h_{uz} .
The outputs from the unsaturated zone define the inputs in groundwater and the concentration in groundwater is calculated by dividing the total inputs by the groundwater volume.

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