Appendix A Model formulation

In this Appendix, the calculations within the different modules of the Impact Pathway Approach as implemented in the WATSON model are described. First, the mathematical formulation of the environmental fate model is presented including the different types of temporal modes of operations (section A.1). Secondly, the processes constituting either the matrix or perturbation vector elements are formulated (section A.3 through A.6). In section A.7, the equations used in the exposure assessment are given. The equations used during the impact assessment and the monetary valuation are given to the extent not yet documented in the main text in sections A.8 and A.9, respectively.

A.1 Overall modelling approach of the environmental fate model

The water and soil environmental fate model is formulated as an inhomogeneous system of ordinary linear first order differential equations. It is 'inhomogeneous' because there is a 'perturbation' term in the differential equations that neither contains the dependent variable (here: concentration) nor its derivative(s) and that is not zero. This perturbation term describes the exogenous inputs from outside the model's scope (i.e., emissions from technosphere, depositions from air, possibly also import via advection from outside the model's scope). The differential equations are called 'first order ordinary' since they only have the first derivative in one variable (here: time).[35] The differential equations are 'linear' as they are linear combinations of the dependent variable and its derivatives.

Note that in the following symbols will be employed that are only used in this section (i.e., A.1 including sub-sections) and are not given in Appendix D.

Assuming that the perturbation term is independent of time one can write the ordinary differential equation (ODE) system in matrix notation as follows:

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[35] If there were different derivatives with respect to more than one variable (e.g., time t and space x, y and/or z) one would have to deal with partial differential equations.

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

where

A	:	coefficient matrix of dimension n x n [m^3/s]
$\vec{b}$	:	perturbation vector of dimension n with exogenous inputs like atmospheric deposition or direct emissions to the compartments [kg/s]
$\vec{c}$	:	concentration vector of dimension n [kg/m^3]
t	:	time [s]
$\vec{v}$	:	volume vector of dimension n [m^3].

There are two solutions of this ODE system implemented: steady-state and dynamic. For computational efficiency reasons, WATSON in both cases tries to subdivide the overall environmental fate matrix in linearly independent sub-matrices before further solving the set of differential equations. In case no air compartment and no marine environment are considered, the different river catchments will constitute linearly independent sets of differential equations that are treated one after the other.

Note that the volume vector only occurs on the left hand side of equation (A-1). For the steady-state solution, it is irrelevant (see below). For the dynamic solution, however, all volumes need to be known in order to solve for the concentration vector. Within WATSON, the matrix A as well as the perturbation vector b are, therefore, divided by the respective volume vector in any case.

A.1.1 Steady-state solution

In particular for sustainability questions, one may want to know what environmental concentrations will occur if a society (or national economy) proceeds at a certain emission level. For this, the steady-state solution can be computed. Steady-state means that there is no concentration change in time (any more), given a constant and continuous emission into the modelled system. Eq. (A-1) hence becomes:

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

Overall the matrix of a spatially-resolved environmental fate model is rather sparse, i.e., contains many zero-elements. This is because not all compartments are interconnected. Thus, only routines based on sparse linear algebra are implemented for the matrix inversion. These make use of the coordinate storage scheme. The routines for sparse matrix inversion are taken from the NAG C library (mark 6). These routines are iterative methods trying to determine the solution through a sequence of approximations until some user-specified termination criterion is met or until some pre-defined maximum number of iterations has been carried out. In order to decrease the number of iterations required for convergence, a preconditioner is often used that is mandatory for the inversion routines as used here. Preconditioning matrices are based on incomplete factorization, in this case incomplete Lower-Upper (LU) factorization. In order to increase the accuracy indicated by the number of pivot modifications, the preconditioning matrices are allowed to become less sparse by increasing the level of fill successively. For details, refer to the NAG C library (mark 6) documentation. Due to the fact that the NAG C library (mark 6) does not contain a routine to invert a sparse matrix as a whole in one step (so-called matrix-matrix operations or Level-3 Basic Linear Algebra Subprograms (BLAS)), each row is successively inverted in a matrix-vector operation (Level-2 BLAS). Due to the fact that one iterative method for the inversion of nonsymmetric linear systems cannot cope with any matrix equally well, different methods and options are implemented that are tried successively if the former try did not result (e.g., an infinite value or an internal error occurred). Without explaining these methods, it shall be stated here that the following methods are tried one after the other while also varying between the inversion of the sparse matrix itself and its transpose for one method: the stabilized bi-conjugate gradient method, the restarted generalized minimum residual method, and the conjugate gradient squared method. The interested reader is referred to the NAG C library (mark 6) documentation and the references given therein.

In some cases, the numerical stability of these methods is not assured if the matrix is ill-conditioned. One way to address this issue is to rescale the matrix (cf. Heijungs and Suh, 2002). Thus, before trying to invert the matrix the minimum and maximum values per row are defined in absolute terms from which the geometric mean is built. The different matrix elements of each row are then divided by the respective resulting value prior to inverting this rescaled matrix. Before the elements of the inverse are stored, the values are back transformed accordingly.

It depends on the removal rates from the system when a substance will reach the steady-state situation. With very persistent substances like heavy metals, the steady-state situation will only be reached after some hundred or even thousands and more years given the potentially very long residence times of these

contaminants, for example, in soils (Alloway et al., 1996). Principally, possible removal rates are degradation or ultimately mineralization, radioactive decay and export to beyond the model's scope.

For pulse emission situations (like in LCA), the steady-state solution may also serve for assessing time-integrated exposures as shown by Heijungs (1995). This, however, depends on the time after which the following key assumption/ condition becomes true:

$$\lim_{t \to \infty} e^{t \cdot A} = 0 . \tag{A-3}$$

If it is really only after millennia or longer that this condition becomes true (e.g of very persistent substances) it is questionable to what extent the calculated time-integrated exposures and consequently impacts are valuable for decision-making purposes.

A.1.2 Dynamic solution

There are principally two ways to arrive at a dynamic solution: analytic and numeric. As was demonstrated for multimedia models (Brandes et al., 1996; Heijungs, 2000; van Eijkeren, 2002), there is an analytical solution to Eq. (A-1) containing a matrix exponential.

$$\vec{c} = e^{t \cdot A'} \times \vec{c}_0 + -A'^{\,-1} \times (I - e^{t \cdot A'}) \times \vec{b}' \tag{A-4}$$

where

A' : coefficient matrix A multiplied by the inverse of the volume vector v, dimension n x n [1/s]

$\vec{b}'$: perturbation vector b multiplied by the inverse of the volume vector v, dimension n [kg/m^3/s]

$\vec{c}$: vector containing the concentrations at a certain time t [kg/ m^3]

$\vec{c}_0$: vector containing the initial concentrations [kg/m^3]

I : identity matrix of dimension n x n; diagonal elements are 1, off-diagonal elements are zero

t : time for which concentrations are computed [s].

In order to solve this matrix exponential, one would need to find the value to which it converges for the following series:

$$e^{A'} = \sum_{n=0}^{\infty} \frac{1}{n!} \cdot A'^n \approx \sum_{n=0}^{m_{convergence}} \frac{1}{n!} \cdot A'^n . \tag{A-5}$$

This might be very resource-intensive for systems where the matrix A has a dimension of several hundred or even thousands. Matrix A can be rewritten as the product of its eigenvector matrix (P) times the diagonal matrix with eigenvalues λ_i (D) times the inverse of the eigenvector matrix (P^{-1}):

$$A' = P \times D \times P^{-1} . \tag{A-6}$$

The matrix exponential hence becomes:

$$\begin{aligned} e^{t \cdot A'} &= \sum_{n=0}^{\infty} \frac{1}{n!} \cdot t^n \cdot A'^n = \sum_{n=0}^{\infty} \frac{1}{n!} \times P \times t^n \times D^n \times P^{-1} \\ &= P \times \left(\sum_{n=0}^{\infty} \frac{1}{n!} \cdot t^n \cdot D^n \right) \times P^{-1} = P \times e^{t \cdot D} \times P^{-1} \end{aligned} \tag{A-7}$$

and, thus, the overall analytical solution can be written as:

$$\vec{c} = P \times e^{t \cdot D} \times P^{-1} \times \vec{c}_0 - P \times D^{-1} \times (I - e^{t \cdot D}) \times P^{-1} \times \vec{b}' . \tag{A-8}$$

The solution of the matrix exponential consequently simplifies to computing the eigenvalues and eigenvectors (and its inverse matrix) as well as the matrix exponential of the diagonal matrix of the eigenvalues. The latter can be facilitated according to:

$$e^{t \cdot D} = \begin{bmatrix} e^{t \cdot \lambda_1} & 0 & \cdots \\ 0 & e^{t \cdot \lambda_2} & \cdots \\ \cdots & \cdots & \cdots \end{bmatrix} . \tag{A-9}$$

However, there might be two drawbacks to the analytic solution of the ODE system. First it needs to be ensured that the matrix is 'well conditioned' so that it is diagonalisable[36] which might not always be the case. Second - and more importantly - it should be made sure that the eigenvalues for the analytic solution are calculated with a high degree of accuracy (i.e., preferably analytically as opposed to by means of numeric methods). Rounding and the tolerance allowed in the numeric derivation of the eigenvalues may produce small but significant inaccuracies in the eigenvalues which might have a major influence on the concentration computations.

In order to find out whether the accuracy of the analytic solution is sufficient, the analytic solution of a two-compartment system was compared to the solution given by a numeric method (Adams method, see below) with the highest tolerance for which a computation could have been successfully performed. The results were identical. Due to computation time reasons, the analytic solution is preferred. For the case that the eigenvalues of the matrix are complex, however, the numeric solution is also implemented. The way how the numeric solution is implemented is described in the following.

When numerically solving an ODE system, one must be aware that these systems could be 'stiff'. If a system is stiff and one wants to be computationally efficient, one needs to adjust the step length to that process ruling 'at the moment'/working point. A system is stiff if the processes involved have substantially different dynamics with respect to the different process rates. An indicator for this is if the eigenvalues have very different negative real parts. In order to decide whether an ODE system is stiff, the following stiffness measure is used:

$$S = \frac{\max_j (|\Re\lambda_j|)}{\min_j (|\Re\lambda_j|)}. \qquad \text{(A-10)}$$

This stiffness measure can obtain values as big as 10^6. There are different perceptions of what is the threshold for stiff systems. As a default a value of 500 is assumed here. This value can be changed by the user.

Depending on the stiffness of the ODE system, two different numeric solution methods[37] are implemented (NAG C library, mark 6):

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[36] A matrix of dimension n is 'well conditioned' if the n eigenvectors are linearly independent. Distinct eigenvalues will ensure linear independence of eigenvectors, but there are cases when degenerate (repeated) eigenvalues give rise to linearly independent eigenvectors.

- for stiff systems: variable-order, variable-step method implementing the Backward Differentiation Formulae (BDF) provided with the Jacobian of the system which is identical to the coefficient matrix, and
- for non-stiff systems: variable-order, variable-step Adams method.

In the NAG documentation of the two numeric methods, it is highly recommended to vary the tolerance before accepting a result. Therefore, if the user has specified to automatically adjust the tolerance for the methods then the computation is started with the default tolerance value (or the tolerance value of a former computation for the scenario-pollutant computation if existent). If a solution was successfully computed, the tolerance is tightened by one order of magnitude and the computation is done again. This is done until an error condition occurs (errors: "the tolerance value is too small for the function to take an initial step" or "the tolerance value is too small for the function to make any further progress across the integration range"). Without giving notice of this error to the user, the results of the last run that was successfully completed are then saved. If the first tolerance value is already too strict, it is loosened by four orders of magnitude and tightened consecutively as described above.

Both methods also require to set the type of (local) error and hence step size control. There are three types to choose from:

1. relative: error requirement is in terms of the number of correct significant digits,
2. absolute: error requirement is in terms of the number of correct decimal places, or
3. mixed: error requirement is a mixture of the two types stated above.

The NAG C library recommends the relative option for the BDF whereas it strongly suggests to use the mixed option for the Adams method. However, in a comparison of the two methods for a system of two equations both methods only yielded similar results when using the same type of step size control. Hence, it was chosen to use the mixed option for both methods.

A.1.3 Dynamic solution until a certain fraction of the steady-state solution

Some substances persist a very long time span in the environment. As was stated above, the steady-state solution might serve as an indicator of whether a certain emission level is sustainable. If such a condition will only occur in many thou-

[37] For more details on the respective methods please refer to numeric method maths books.

sands of years or more, however, the steady-state solution - even if used for time-integrated exposures - may not be as meaningful any more at least in the context of policy decision-making. Therefore, WATSON allows the user to calculate the time span until a certain percentage of the steady-state solution is reached. This feature is implemented for the analytic as well as for the numeric solution.

One main distinction between the analytic and the numeric solution approaches is that the analytic solution is done in discrete steps. If the required percentage of the steady-state solution is reached or exceeded, the time is assessed by linearly interpolating between the results of the latest and the previous time step. This might lead to overestimations especially for the concentrations computed for the first time step if initial values are equal to zero. The time steps are different for the time span for which the dynamic solution is calculated and for the time afterwards until the maximum time limit. For the first interval the time steps are equal to the time steps specified by the user. For the second interval the time steps are set according to the constraints set by the user ('default settings'): The remaining time is divided into a number of time steps of between two (user-changeable) default minimum and maximum values also taking a 'threshold time step' into account. If the remaining time divided by the minimum time step yields a larger value than the 'threshold time step' the time step is adjusted to have at most the maximum allowed amount of time steps at a time span close to the 'threshold time step' if possible.

In contrast to the analytic solution, the numeric methods implemented (see section A.1.2) compute results continuously. Therefore, no interpolation between results is necessary. With both numeric methods, apart from specifying the end of the integration interval, the user can supply a function for setting another cut-off criterion. This is used when computing the 'time to steady-state' (or a fraction of it) by checking whether the concentrations in all compartments have reached the specified fraction (> 0-100 %) of the steady-state solution or whether the specified time limit has been reached.

If the time limit is reached for both the analytic and the numeric approach, the percentage of the steady-state solution reached until this moment is saved alongside with the time limit.

A.2 Partitioning of substances and equilibrium distribution coefficients

The Mackay-type multimedia models rely to a rather large extent on the equilibrium partitioning of substances between different phases (Mackay, 1979, 1991). In these box models, the world is separated into homogeneous compartments on which the mass balance is based. A substance in either of the distinguished com-

partments is assumed to be in equilibrium between the different phases present, i.e., the solid phase which may consist of lipophilic (i.e., living or non-living organic matter) and non-lipophilic phases, the aqueous phase and potentially a gas phase. Several processes will only involve one of these phases. In order to allow processes only to involve a substance's amount present in just one of these phases within a compartment, the concept of the *equilibrium distribution coefficient* between the bulk compartment and the respective single phase may be used (Brandes et al., 1996) which builds on the substance-dependent partitioning coefficients (cf. section C.1).

In order to define the equilibrium distribution coefficient, the rule is followed here to relate the concentration of a substance in the bulk compartment to its concentration in the minority phases. Such minority phases are for example for soils the aqueous and gas phases, and for water compartments the suspended matter phase. For sediments in particular, the definition of a minority phase is difficult due to the high vertical variability in the prevalence of its constituents. At present, water is still the dominant phase according to the 'volume fraction that is solid phase' used (cf. section B.5.4). Nevertheless, sediments are treated in the same way as soils.

Note that in this document the term 'water' is normally used for the water compartment whereas 'aqueous' is used for the water phase in a compartment. Notable exceptions are the established names of parameters such as air-water partitioning coefficient K_{aw}, octanol-water partitioning coefficient K_{ow}, or the solid-water partitioning coefficient K_{sw}.

A.2.1 Bulk compartment-aqueous phase or solid phase equilibrium distribution coefficients

Following the rule as stated above, the equilibrium distribution coefficients for the compartments with a significant solid phase relate the bulk phase concentration to the aqueous phase or potentially gas phase concentration according to:

$$ED_{\text{bulk/aqueous.p}} = \frac{C\_w/v_{\text{bulk}}}{C\_w/v_{\text{aqueous phase}}} = (fr\_V_{\text{aqueous phase}} \cdot C\_w/v_{\text{aqueous phase}} + fr\_V_{\text{solid phase/bulk}} \cdot C\_w/v_{\text{solid phase}} + fr\_V_{\text{gas phase/bulk}} \cdot C\_w/v_{\text{gas phase}}]/C\_w/v_{\text{aqueous phase}} \quad \text{(A-11)}$$

where

C_w/v : concentration in the bulk compartment or in one of its phases [kg per m^3]

ED : equilibrium distribution coefficient relating the bulk compartment concentration to that of the aqueous phase [-]

fr_V : volume fraction of soil that is solid or gas phase [m^3_{phase} per $m^3_{bulk\ compartment}$].

Note that in the following the volume fraction of aqueous phase is expressed as the complement of the sum of those of the solid and gas phase.

For surface compartments with a substantial gas phase, i.e., soils, the bulk compartment-water phase equilibrium distribution coefficient, thus, becomes:

$$ED_{bulk/aqueous,p} = (1 - fr\_V_{solid\ phase\ bulk} - fr\_V_{gas\ phase\ bulk}) + fr\_V_{solid\ phase\ bulk} \cdot K_{sw,p} \cdot \rho_{solid\ phase} + fr\_V_{gas\ phase\ bulk} \cdot K_{aw,p} \quad \text{(A-12)}$$

where

ED : equilibrium distribution coefficient relating the bulk compartment concentration to that of the aqueous phase [-]

fr_V : volume fraction of soil that is solid or gas phase [m^3_{phase} per $m^3_{bulk\ compartment}$]

K_{aw} : air-water partitioning coefficient or dimensionless Henry's law constant of substance *p* [-] (defined by Eq. (C-3))

K_{sw} : solid-water partitioning coefficient of substance *p* that may depend on pH or the organic carbon content of the respective compartment [$kg/kg_{solid\ phase}$ per kg/m^3_{water}] (defined in section C.1.1)

ρ : density of the solid phase [$kg_{solid\ phase}$ per $m^3_{solid\ phase}$].

For sediment and ground water (if distinguished), principally only the volume fraction of the gas phase becomes zero. Eq. (A-12) thus reduces to:

$$ED_{bulk/aqueous,p} = (1 - fr\_V_{solid\ phase\ bulk}) + fr\_V_{solid\ phase\ bulk} \cdot K_{sw,p} \cdot \rho_{solid\ phase} \quad \text{(A-13)}$$

The respective bulk-solid phase equilibrium distribution coefficient of sediments and ground water can be derived based on the corresponding bulk-aqueous phase equilibrium distribution coefficient:

$$ED_{\text{bulk/solid,p}} = \frac{(1 - fr\_V_{\text{solid phase/bulk}})}{K_{\text{sw,p}} \cdot \rho_{\text{solid phase}}} + fr\_V_{\text{solid phase/bulk}} = \frac{ED_{\text{bulk/aqueous,p}}}{K_{\text{sw,p}} \cdot \rho_{\text{solid phase}}} \quad \text{(A-14)}$$

The parameter $\rho_{\text{solid phase}}$ may be chosen by the user to differ for the land uses arable soil, pasture, semi-natural ecosystems, non-vegetated land and sediment based on data derived from a GIS dataset (Batjes, 1996) and the differentiation into streams and large lakes (cf. Eq. (B-10)).

A.2.2 Bulk water-suspended matter or aqueous phase equilibrium distribution coefficients

As discussed in section 6.1, the freshwater compartment only consists of water and suspended solids. The concentration in the bulk water compartment is defined accordingly:

$$C\_w/v_{\text{bulk water,p}} = C\_w/v_{\text{solid phase,p}} \cdot fr\_V_{\text{solid phase/bulk}} + C\_w/v_{\text{aqueous phase,p}} \cdot (1 - fr\_V_{\text{solid phase/bulk}}) \quad \text{(A-15)}$$

where

C_w/v : concentration in the bulk compartment or in one of its phases [kg per m^3]

ED : equilibrium distribution coefficient relating the bulk compartment concentration to that of the aqueous phase [-]

fr_V : volume fraction of soil that is solid phase [$m^3_{\text{solid phase}}$ per $m^3_{\text{bulk compartment}}$] (defined in section 5.1.3).

Relating the bulk concentration to the solid phase concentration yields the respective equilibrium distribution coefficient:

$$ED_{\text{bulk/solid,p}} = \frac{C\_w/v_{\text{bulk water,p}}}{C\_w/v_{\text{solid phase,p}}} \tag{A-16}$$

$$= fr\_V_{\text{solid phase/bulk}} + \frac{C\_w/v_{\text{aqueous phase,p}} \cdot (1 - fr\_V_{\text{solid phase/bulk}})}{C\_w/v_{\text{solid phase,p}}}$$

$$= fr\_V_{\text{solid phase/bulk}} + \frac{(1 - fr\_V_{\text{solid phase/bulk}})}{K_{\text{sw,p}} \cdot \rho_{\text{suspended matter}}}$$

$$= \frac{1}{ED_{\text{suspended matter/bulk water,p}}}$$

where

ED : equilibrium distribution coefficient relating the bulk compartment concentration to that of the solid phase (or relating the suspended matter phase to the bulk water compartment concentration) [-]

fr_V : volume fraction of freshwater that is solid phase [$m^3_{\text{solid phase}}$ per $m^3_{\text{bulk compartment}}$] (computed according to Eq. (A-17))

K_{sw} : solid-water partitioning coefficient of substance *p* [$kg/kg_{\text{solid phase}}$ per kg/m^3_{water}]

ρ : density of the solid phase [$kg_{\text{solid phase}}$ per $m^3_{\text{solid phase}}$].

$$fr\_V_{\text{solid phase/bulk}} = \frac{C\_w/v_{\text{suspended matter}}}{\rho_{\text{suspended matter}}} \tag{A-17}$$

The bulk water-aqueous phase equilibrium distribution coefficient (for diffusive intermedia exchange between water compartment and sediment compartment) can be computed analogously. Here, it is defined based on the bulk water-solid phase equilibrium distribution coefficient according to:

$$ED_{\text{bulk/aqueous,p}} = ED_{\text{bulk/solid,p}} \cdot K_{\text{sw,p}} \cdot \rho_{\text{suspended matter}} \cdot \tag{A-18}$$

A.3 Environmental fate process formulations

In the following, the different environmental fate processes are described for which formulae are provided by WATSON. These can be combined in different ways as a so-called *process set* (cf. section 5.1).

A.3.1 Degradation

Degradation or rather chemical transformation may occur principally via biotic or abiotic processes (e.g., Schnoor, 1996; European Commission, 2003b). Such processes comprise hydrolysis, photolysis, biodegradation and co-metabolism.

A better notion for 'degradation' which might imply that a substance has been fully mineralised and does not pose any harm any longer could be 'chemical transformation' or 'inactivation'. In particular the latter notion might well be suited to comprise all processes that keep toxic substances from becoming effective (again).

Except for photolysis at the interface between air and the ground, degradation in the terrestrial and aquatic environment is assumed to occur in all compartments with liquid water, i.e., freshwater body (*i*: w), freshwater sediment (*i*: ws), impervious surface (*i*: u), non-vegetated land (*i*: b), (semi-)natural ecosystems (*i*: n), pasture/grassland (*i*: p) and arable land (*i*: ag), and is formulated according to:

$$k_{i,\,\mathrm{deg}}(p,i,z) = A(z)\cdot fr\_\mathrm{A}(i,z)\cdot d(i,z)\cdot\frac{\ln(2)}{t_{1/2}(p,i)} \qquad \text{(A-19)}$$

where

A	:	area of zone z [m^2] (defined in section B.2)
d	:	depth of the compartment i in zone z [m] (defined in sections 5.1 and B.4.3)
fr_A	:	area fraction of compartment i in zone z [-] (defined in section B.3)
k	:	process rate for degradation [m^3 per s]
$t_{1/2}$	:	degradation half-life of substance p in compartment i [s^{-1}].

Note that the degradation half-life aggregates the different chemical transformation processes occurring simultaneously in one compartment.

A.3.2 Radioactive decay

Another process which leads to the disappearance of a modelled substance may be radioactive decay. In this case, single isotopes are addressed since the radioactive decay may indeed lead to a change in the nuclear composition of an atom but the number of protons might stay the same.

Radioactive decay is formulated equivalently to degradation but is not confined to compartments in which liquid water occurs, thus, *i* may correspond to any compartment distinguished:

$$k_{i,\,\mathrm{decay}}(p,i,z) = A(z)\cdot fr\_\mathrm{A}(i,z)\cdot d(i,z)\cdot\frac{\ln(2)}{t_{1/2}(p,i)} \qquad \text{(A-20)}$$

where

A	:	area of zone z [m^2] (defined in section B.2)
d	:	depth of the compartment i in zone z [m] (defined in sections 5.1 and B.4.3)
fr_A	:	area fraction of compartment i in zone z [-] (defined in section B.3)
k	:	process rate for radioactive decay [m^3 per s]
$t_{1/2}$	:	decay half-life of radionuclide p in compartment i [s^{-1}].

A.3.3 Water soil erosion

Generally, erosion may be defined as "wearing away and transport of the soil by running water, glaciers, wind or waves" (Deutsches Nationalkomitee für das internationale Hydrologische Programm (IHP) der UNESCO und das Operationelle Hydrologische Programm (OHP) der WMO, 1998, p. 54). Here, only the erosion by water is modelled which is in line with all of the reviewed multimedia models (cf. sections 3.1 and 4.2.2).

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

As indicated above, when assessing soil erosion from a soil or agricultural science perspective, usually only the loss at a given site is of interest which leads

especially to a reduced soil fertility or production capacity (Morgan, 1999). As a consequence, very few of the erosion models predict how much of the soil arrives at adjacent areas or compartments. Attempts have been made to relate the results of the RUSLE to inputs into streams for example by means of the sediment delivery ratio concept (Umweltbundesamt, 1999). However, the RUSLE is still too data demanding at the regional scale and the sediment delivery ratio concept is highly questioned (Walling, 1983).

No transport of eroded soil from one terrestrial compartment to another is considered in WATSON for two reasons: (a) the compartments distinguished are assumed to be homogeneous implying that re-distribution of eroded soil within one compartment is irrelevant and (b) there is a lack of information about the situation of one compartment relative to another (cf. section 4.2.2). Rather, only the transport from the terrestrial environment into surface freshwater bodies is assessed. Zaslavsky (1979) quoted by Golubev (1982) estimated that only 10 % of the gross erosion is transported to the larger rivers, the remainder mostly being only re-distributed in the terrestrial environment (e.g., deposited on the lower parts of slopes). Walling (1983) estimates that only about 0.1 % to 38 % of the gross soil loss reach the rivers' outlets and are represented in the so-called sediment yield (see section B.5.3).

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

Due to the potentially low erosion rate on permanently vegetated areas like pastures/grassland and semi-natural ecosystems, water soil erosion is substantially reduced for these compartments (cf. section B.5.3). It is clear that this assumption is not appropriate in any situation. It is considered a justified first approximation, however, as this distinction is in line with both the considerably lower crop management factor of the Universal Soil Loss Equation (USLE) for forest and pasture soils (e.g., Golubev, 1982; Morgan, 1999; Umweltbundesamt, 1999) as well as with existing forest soil models (e.g., Reinds et al., 1995). Allowing the water soil erosion rate only to vary by compartments is, furthermore, supported by the present paucity or rather absence of regional erosion estimates or modelling capabilities at the regional scale (Bach et al., 2001) for the whole of Europe.

The process of water soil erosion which is allowed to occur on arable land (*i*: ag), pastures (*i*: p), semi-natural ecosystems (*i*: n) and non-vegetated land (*i*: b) is calculated according to:

$$k_{i\text{-}w,\,\text{erosion}}(z,i) = A(z) \cdot fr\_\text{A}(i,z) \cdot v_{\text{erosion}}(i) \qquad \text{(A-21)}$$

where

A	:	area of zone z [m^2] (defined in section B.2)
fr_A	:	area fraction of compartment i in zone z [-] (defined in section B.3)
k	:	process rate for water soil erosion [m^3 per s]
v	:	erosion velocity of compartment i [m per s] (defined in Table 5-7).

A.3.4 Overland flow

Overland flow or rather saturated overland flow (Mosley and McKerchar, 1993) may be defined as "(f)low of water over the ground before it enters a definite channel" (Deutsches Nationalkomitee für das internationale Hydrologische Programm (IHP) der UNESCO und das Operationelle Hydrologische Programm (OHP) der WMO, 1998, p. 109). This process is contained in many multimedia models (cf. Table 5-4).

There are different causes why water does not penetrate the ground but flows over it instead (Rawls et al., 1993). The probably most important example is the so-called Hortonian overland flow (Rodhe and Killingtveit, 1997) which occurs when the infiltration capacity of a soil is exceeded by the rain intensity.

From a runoff formation point of view, i.e., the formation of that "part of the precipitation that appears as streamflow" (Deutsches Nationalkomitee für das internationale Hydrologische Programm (IHP) der UNESCO und das Operationelle Hydrologische Programm (OHP) der WMO, 1998, p. 109), one may want to distinguish between the three components (a) saturated overland flow, (b) interflow and (c) baseflow or return flow from ground water (Mosley and McKerchar, 1993). While vertical percolation of water through a soil column is mostly responsible for ground water recharge and, thus, contributes or sustains the baseflow, interflow passes through the subsurface similar to the baseflow but is quicker resembling more the dynamics of the saturated overland flow. This is also why interflow together with saturated overland flow are also referred to as 'quickflow' (Mosley and McKerchar, 1993).

The data available for the water balance within WATSON allow the distinction of ground water recharge from the overall runoff (cf. section B.5.2). As a result, the process of overland flow is extended to comprise the whole water undergoing 'quickflow', i.e., including interflow. Although interflow water may

pass the subsurface at depth below 30 cm (corresponding to the default soil compartment depth; cf. section 5.1.2), it is assumed here that it does not leave the topsoil towards the deeper subsurface.

One may argue that the extended overland flow process is responsible for the transport of pore waters. However, overland flow is perceived here to lead to an equilibration of substances contained in soils with water flowing at the surface or near the surface ('interflow') whereas the process of water soil erosion is responsible for soil pore water displacements (cf. section A.3.3). Due to the fact that the compartments are rather large in this regional scale environmental fate modelling approach, the contact time of the waters undergoing quickflow is assumed to be sufficiently long for the substances to reach equilibrium, noting that this will not be the case for any substance.

The extended overland flow process for the pervious compartments, i.e., arable land (*i*: ag), pastures (*i*: p), semi-natural ecosystems (*i*: n) and non-vegetated land (*i*: b), is defined as:

$$k_{i\text{-}w,\,\text{overland flow},\,pH|C_{org}}(p,i,z) = \mathrm{A}(z)\cdot fr\_A(i,z)\cdot \frac{v_{\text{runoff}}(z)\cdot fr\_v_{\text{quick flow/runoff}}(z)}{ED_{\text{bulk aqueous},\,pH|C_{org}}(p,i,z)} \qquad \text{(A-22)}$$

where

A : area of zone z [m^2] (defined in section B.2)

ED : equilibrium distribution coefficient of a substance p of the respective compartment i of zone z that may depend on a compartment's pH or organic carbon content [-] (defined in section A.2)

fr_A : area fraction of compartment i in zone z [-] (defined in section B.3)

fr_V : fraction of runoff being quickflow in zone z [-] (defined in section B.5.2)

k : process rate for the extended overland flow [m^3 per s]

v : runoff in zone z [m per s] (defined in section B.5.2).

For the impervious terrestrial compartments, one has to further distinguish between glaciers and sealed areas. Whereas precipitation to glaciers is assumed to be solid ('snow') which only start to flow substantially upon melting (cf. section A.3.5), saturated overland flow (in its strict sense) is modelled for impervious surfaces according to:

$$k_{u-w,\,\text{overland flow},\,\text{pH}|\,C_{org}}(p,u,z) = A(z)\cdot fr\_A(u,z)\cdot \frac{v_{\text{runoff}}(z)}{ED_{\text{bulk/aqueous},\,\text{pH}|C_{org}}(p,u,z)} \quad \text{(A-23)}$$

where

A : area of zone z [m^2] (defined in section B.2)

ED : equilibrium distribution coefficient of a substance p of the respective compartment i of zone z that may depend on a compartment's pH or organic carbon content [-] (defined in section A.2)

fr_A : area fraction of compartment i in zone z [-] (defined in section B.3)

k : process rate for overland flow from impervious surfaces [m^3 per s]

v : runoff in zone z [m per s] (defined in section B.5.2).

A.3.5 Ice melt

As with soils, the assumption of homogeneity is unlikely to be true for glaciers (Baumgartner and Liebscher, 1990). As it seems that so far nobody has ever addressed the influence of glaciers on the overall fate of persistent pollutants in a multimedia context, a simple formulation has been adopted to start with. For the reasoning why glaciers are distinguished at all, refer to section 5.1.11.

The process ice melt leads to the release of flowing water by glaciers and consequently of substances contained in the ice which are delivered to the freshwater compartment:

$$k_{gl-w,\,\text{ice melt}}(z,gl) = A(z)\cdot fr\_A(gl,z)\cdot \frac{d(gl,z)}{t_{\text{residence}}(gl)} \quad \text{(A-24)}$$

where

A : area of zone z [m^2] (defined in section B.2)

d : depth of glaciers gl [m] (defined in section 5.1.11)

fr_A : area fraction of compartment i in zone z [-] (defined in section B.3)

k : process rate for ice melt [m^3 per s]

$t_{residence}$: residence time of water in glaciers *gl* [s].

The rate by which this process takes place is defined according to the residence time. The residence of water in Alpine glaciers amounts to 100 years according to Table 9.1 in Baumgartner and Liebscher (1990) which is adopted here and which is assumed to be also valid for the other glaciers occurring in the modelled area.

A.3.6 Matrix leaching

The process matrix leaching transports substances dissolved (at equilibrium) in soil pore water flowing towards the subsurface. This flowing water constitutes the ground water recharge and finally the baseflow in the runoff formation process (Mosley and McKerchar, 1993, cf. section A.3.4). The matrix leaching process is defined for pervious soils, i.e., arable land (*i*: ag), pastures (*i*: p), semi-natural ecosystems (*i*: n) and non-vegetated land (*i*: b):

$$k_{i\text{-}gw,\,\text{leaching},\,\text{pH}|C_{org}}(z,i,p) = A(z)\cdot fr\_\text{A}(i,z)\cdot \frac{(1-fr\_v_{\text{quick flow/runoff}}(z))\cdot v_{\text{runoff}}(z)}{ED_{\text{bulk/aqueous},\,\text{pH}|C_{org}}(p,i,z)} \qquad \text{(A-25)}$$

where

A : area of zone *z* [m^2] (defined in section B.2)

ED : equilibrium distribution coefficient of a substance *p* of the respective compartment *i* of zone *z* that may depend on a compartment's pH or organic carbon content [-] (defined in section A.2)

fr_A : area fraction of compartment *i* in zone *z* [-] (defined in section B.3)

fr_V : fraction of runoff being quickflow in zone *z* [-] (defined in section B.5.2)

k : process rate for matrix leaching [m^3 per s]

v : runoff in zone *z* [m per s] (defined in section B.5.2).

An example of water percolating through soil that is not at equilibrium with the soil matrix is presented in section A.3.7.

If a ground water compartment was distinguished, the process 'ground water exfiltration with sorption' would be formulated correspondingly connecting the ground water compartment to the surface freshwater compartment of the same zone.

A.3.7 Considering vertical substance transport in soils due to stochastic processes

Many soil parameters are conceived as the realization of a random spatial field (e.g., Richter et al., 1996) which is due to the rather stochastic soil behaviour with respect to water and substance transport. A prominent example for a stochastic transport process within soils is preferential flow (Gish and Shirmohammadi, 1991). This is a non-equilibrium process in terms of both water flow (Beven, 1991; 'preferential flow' strictly speaking) and solutes entrained therein (Helling and Gish, 1991; Luxmoore, 1991; Stagnitti et al., 1995; Schwarz and Kaupenjohann, 2000; 'preferential transport'). This process is more the rule than the exception (Flury, 1996) and may have different causes (Wittig et al., 1985; Helling and Gish, 1991; Steenhuis and Parlange, 1991; Schwarz and Kaupenjohann, 2000). It even also applies to atmospheric deposition to forests (Wittig et al., 1985; Chang and Matzner, 2000).

As stated in Steenhuis and Parlange (1991), the amount of water percolating through the top soil layer may be distinguished into preferential and matrix flow which is adopted here.

Another stochastic process is colloidal transport (Jarvis et al., 1999; Noack et al., 2000) which can be considered to be part of the process 'preferential transport' defined by Eq. (A-27). This is also relevant especially for those trace elements which bind to organic matter such as lead and cadmium (Bergkvist et al., 1989).

Reduced matrix leaching due to preferential flow

This process is introduced in order to take into account that a portion of the wet atmospheric deposition is directly transferred to the subsurface soil layers for permeable terrestrial land uses (cf. section A.6.4). The amount of water undergoing this process does not have the time to fully equilibrate with the soil matrix ('non-equilibrium transport', Schwarz and Kaupenjohann, 2000) allowing to distinguish the rain water from the soil pore water in equilibrium with the soil matrix (Luxmoore, 1991). As a consequence, it is assumed here that the preferential flow portion of the wet precipitation is not available to matrix leaching. The equation is, therefore, introduced to subtract the amount of water undergoing preferential flow.

The reduced matrix leaching process is defined for pervious compartments, i.e., arable land (*i*: ag), pastures (*i*: p), semi-natural ecosystems (*i*: n) and non-vegetated land (*i*: b), as follows:

$$k_{i\text{-}gw,\ \text{pref flow},\ \text{pH|C}_{org}}(z, i, p) = -A(z) \cdot fr\_\text{A}(i, z) \cdot \frac{v_{\text{rain}}(z) \cdot fr\_v_{\text{pref flow rain}}(z)}{ED_{\text{bulk aqueous, pH|C}_{org}}(p, i, z)} \qquad \text{(A-26)}$$

where

A : area of zone z [m^2] (defined in section B.2)

ED : equilibrium distribution coefficient of a substance p of the respective compartment i of zone z that may depend on a compartment's pH or organic carbon content [-] (defined in section A.2)

fr_A : area fraction of compartment i in zone z [-] (defined in section B.3)

fr_V : fraction of precipitation undergoing preferential flow in zone z [-] (defined in section B.5.2)

k : process rate for reduced matrix leaching [m^3 per s]

v : precipitation in zone z [m per s] (defined in section B.5.2).

Assuming that preferential flow does not lead to an accelerated movement of a substance already contained in a soil to the subsurface is rather conservative in the sense that preferential flow will carry away some of the dissolved ('displacement of matrix water', cf. Helling and Gish, 1991) and adsorbed phases of substances in soils. Therefore, another process is introduced which is described next.

Preferential transport

Preferential flow may displace part of matrix water (cf. Helling and Gish, 1991). Thus, only subtracting the amount of rainwater immediately undergoing preferential flow may not be sufficient to account for this process (cf. equation (A-26)) as parts of the substance contained in the soil will also be affected. For instance, the amounts of pesticides lost due to this process normally lie in the range of smaller than 0.1 % and 1 % and may reach up to 5 % under worst case conditions (Flury, 1996). When also including colloidal transport, a value for the amount to bypass the top soil layers of 0.1 %, thus, appears to be a reasonable first (conservative) estimate. In order to convert this overall mass balance into a rate, the 0.1 %

are assumed to apply to an annual mass balance meaning that 0.1 % of the annual amount of substances present in the soil reaches the subsurface by preferential transport. The respective rate is, thus, 0.001 per year. One has to note, however, that this rate may be substantially higher for non-degrading substances such as trace elements. However, different volatilisation and adsorption behaviours, for instance, play a role here so that the value is adopted for the time being for any substance until more specific information becomes available.

The preferential transport process is defined for pervious compartments, i.e., arable land (*i*: ag), pastures (*i*: p), semi-natural ecosystems (*i*: n) and non-vegetated land (*i*: b), as follows:

$$k_{i\text{-}gw,\,\text{preferential transport}}(z, i, p) = A(z) \cdot fr\_\text{A}(i, z) \cdot r_{\text{preferential transport}}(p, i) \qquad \text{(A-27)}$$

where

A	:	area of zone z [m^2] (defined in section B.2)
fr_A	:	area fraction of compartment i in zone z [-] (defined in section B.3)
k	:	process rate for the extended overland flow [m^3 per s]
r	:	rate of preferential transport of substance p in compartment i [s^{-1}] (defined in the text above).

A.3.8 Uptake by biota and removal

As described in section 5.2 on plants and 6.2 on freshwater fish, living organisms do not constitute separate compartments in the environmental fate model. In regulatory risk assessments when following rather conservative assessment principles, removal of substances from the environment due to intake by organisms and subsequent consumption by (other) animals or humans is often not considered (e.g., European Commission, 1996a). This causes the environmental media concentrations to be larger due to lower removal rates. In spite of not distinguishing biotic compartments in the environmental fate modelling, a substance's removal across the model's boundary due to uptake by biota followed by harvest or catches, respectively, may still be considered.

The harvest and catch rates are set equivalent to the amounts produced per year. This is because the root uptake by plants as well as bioconcentration by fish are assumed to be in equilibrium with the medium on which the organisms thrive. When assessing the amount removed due to intercepting a part of the atmospheric deposition, the actual time the produce is exposed is also considered (see section A.6.5).

Root uptake by and harvest of belowground produce

As argued in section 5.2, belowground produce can be considered in equilibrium with soil for both organic substances and metals while receiving negligible amounts from aboveground plant parts. In order not to distinguish a separate belowground plant compartment for computational efficiency reasons but still allow for removal of the amount of substances that is contained in the harvested plant parts, a combined process is, thus, formulated here.

Based on the bioconcentration factor for root produce relating bulk dry weight root concentration to bulk dry weight soil concentration (equation 5-20B from United States - Environmental Protection Agency (1998), modified) and the production rate of the root produce, the root uptake by and harvest of belowground produce can be described. Additionally converting the bulk soil (volumetric) concentration into a dry soil (mass-based) concentration the combined process can be written as:

$$k_{i,\,\text{uptake+harvest root crops}} = \frac{1}{fr\_V_{\text{solid phase bulk}}(i) \cdot \rho_{\text{solid phase}}(i,z)} \cdot emp_{\text{BCF, root crops}}(p,r,e) \cdot fr\_w_{\text{solid phase bulk}}(r,e) \cdot BCF\_dw/dw_{\text{root soil}}(p,r,e) \cdot P(r,n) \qquad \text{(A-28)}$$

where

BCF_dw/dw: bioconcentration factor of substance *p* due to root crop *r* uptake from soil [kg_{soil} DW per kg_{plant} DW] (defined in section C.2)

emp : empirical correction factor for equilibrium uptake of substance *p* by belowground produce *r* dependent on the substance's octanol-water partitioning coefficient (K_{ow}) [-]

fr_V : volume fraction of soil that is solid phase [$m^3_{solid\ phase}$ per $m^3_{bulk\ compartment}$] (defined in section 5.1.3)

fr_w : mass fraction of food (*r*) dry matter [kg DW per kg FW] (defined in Table B-22)

k : process rate of root uptake by and harvest of root crops with respect to compartment *i* [m^3 per s]

P : production rate of crop *r* in administrative unit *n* [kg FW per s] (defined as described in section B.6.1)[38]

ρ : density of the solid phase [$kg_{solid\ phase}$ per $m^3_{solid\ phase}$] (defined by Eq. (B-10)).

The empirical correction factor assumes values between 1 and 0.01. According to the recommendations given by United States - Environmental Protection Agency (1998), a value of 1 should be used if log K_{ow} is less than 4 and 0.01 otherwise. As argued in section 5.2.2, an intermediate value of 0.1 for log K_{ow} range from 2 to 4 could additionally be introduced based on the findings by Riederer (1995) and Trapp (2002).

Note that the k-value is representative only for one type of root crop. If there are different types of root crops produced on one agricultural soil compartment and if any of the parameters 'production rate', 'mass fraction of food dry matter', or 'BCF' differs, a sum over the respectively resulting k-values needs to be computed according to (for the explanation of the symbols refer to the equation above):

$$k_{i,\ uptake+harvest\ root\ crops} = \frac{1}{fr\_V_{solid\ phase\ bulk}(i) \cdot \rho_{solid\ phase}(i,z)} \cdot emp_{BCF,\ root\ crops}(p,r,e) \cdot \sum_{x = r_1, r_2, \ldots} [fr\_w_{solid\ phase\ bulk}(x,e) \cdot BCF\_dw/dw_{root:soil}(p,x,e) \cdot P(x,n)] \quad \text{(A-29)}$$

Note that the empirical factor at present does not distinguish between different belowground crops and is, therefore, not contained in the sum. Further note that the production rate needs to be distributed from administrative units (denoted by *n* here) to zones. This is done on an area-weighted basis.

Root uptake by and harvest of aboveground produce for non-volatile substances

As phloem flow for non-essential heavy metals can be disregarded, the concentrations found in aboveground protected produce solely depend on soil concentrations and corresponding uptake. For aboveground exposed produce, the

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[38] The removal will be underestimated based on the amounts produced per year provided by the Food Balance Sheets (FBSs, Food and Agriculture Organization of the United Nations - Statistics Division, 2002a). This is because losses for example between the harvest and the sale are not included in the production data.

contribution by atmospheric deposition needs to be considered additionally (see section A.6.5).[39] Its exposure via root uptake is formulated in the same way as for aboveground protected produce. Note that this process is not formulated for forage taken in for example by cattle. This is mainly because there is no statistical production data available in the FAO statistical database presumably due to the fact that forage is not traded across national borders.

Based on the bioconcentration factor for aboveground produce relating bulk dry weight aboveground protected produce concentration to bulk dry weight soil concentration (equation 5-20B United States - Environmental Protection Agency (1998), modified) and the production rate, the root uptake by and harvest of aboveground produce can be described. Additionally converting the bulk soil (volumetric) concentration into a dry soil (mass-based) concentration, the combined process can be written as:

$$k_{\text{i, uptake+harvest aboveground crops}} = \frac{1}{\begin{array}{l} fr\_V_{\text{solid phase/bulk}}(i) \cdot \rho_{\text{solid phase}}(i,z) \cdot \\ fr\_w_{\text{solid phase/bulk}}(r,e) \cdot \\ BCF\_dw/dw_{\text{plant/soil}}(p,r,e) \cdot P(r,n) \end{array}} \cdot \qquad \text{(A-30)}$$

where

BCF_dw/dw: bioconcentration factor of substance p due to aboveground produce r uptake from soil [kg_{soil} DW per kg_{plant} DW] (defined in section C.2)

fr_V : volume fraction of soil that is solid phase [$m^3_{\text{solid phase}}$ per $m^3_{\text{bulk compartment}}$] (defined in section 5.1.3)

fr_w : mass fraction of food (r) dry matter [kg DW per kg FW] (defined in Table B-22)

k : process rate of root uptake by and harvest of aboveground crops with respect to compartment i [m^3 per s]

P : production rate of crop r in administrative unit n [kg FW per s] (defined as described in section B.6.1)

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[39] In the case of (semi-) volatile substances, diffusive air-plant exchanges may need to be included for exposed produce. In order to consider this process, it is preferred to follow an approach that allows for kinetic, i.e., non-equilibrium transfer at the plant surface. This would make it necessary that a plant compartment is introduced in the environmental fate model.

ρ : density of the solid phase [$kg_{solid\ phase}$ per $m^3_{solid\ phase}$] (defined by Eq. (B-10)).

Again note that the k-value is representative only for one type of aboveground produce. If there are different types of aboveground produce produced on one agricultural soil compartment and if any of the parameters 'production rate', 'mass fraction of food dry matter', or 'BCF' differs, a sum over the respectively resulting k-values needs to be computed according to (for the explanation of the symbols refer to the equation above):

$$k_{i,\ uptake+harvest\ aboveground\ crops} = \frac{1}{fr\_V_{solid\ phase/bulk}(i) \cdot \rho_{solid\ phase}(i,z)} \cdot \sum_{x = r_1, r_2, \ldots} [BCF\_dw/dw_{plant/soil}(p,x,e) \cdot fr\_w_{solid\ phase/bulk}(x,e) \cdot P(x,n)] \quad \text{(A-31)}$$

Note that *r* stands for protected and exposed aboveground produce equally. Further note that the production rate needs to be distributed from administrative units (denoted by *n* here) to zones. This is done on an area-weighted basis.

Uptake by and catch of freshwater fish for non-volatile substances

Similar to the removal by plant harvest, a removal by fish catches is proposed. Based on the bioconcentration factor for fish relating bulk fish concentration to aqueous phase water concentration (equation 5-48, United States - Environmental Protection Agency, 1998) and the production rate, the uptake by and catch of freshwater fish can be described. Additionally converting the bulk water concentration into the aqueous phase concentration of the water compartment, the combined process can be written as:

$$k_{w,\ uptake+catch\ fish} = \frac{1}{Ksw \cdot ED_{bulk/solid} \cdot \rho_{suspendend\ matter}(w,z)} \cdot BCF\_V/fw_{fish/water}(p,r,e) \cdot P(r,n) \quad \text{(A-32)}$$

where

BCF_V/fw : bioconcentration factor of substance *p* due to fish *r* uptake from water [$m^3_{aqueous\ phase}$ per kg_{fish} FW] (defined in section C.2)

ED : bulk water compartment-suspended matter phase equilibrium distribution coefficient [$m^3_{bulk\ compartment}$ per $m^3_{solid\ phase}$] (defined in section A.2)

k : process rate of uptake by and catch of fish in freshwater *w* [m^3 per s]

K_{sw} : solid-water partitioning coefficient [$m^3_{aqueous\ phase}$ per $kg_{solid\ phase}$] (defined in section C.2)

P : production rate of freshwater fish *r* in administrative unit *n* [kg FW per s] (defined as described in section B.6.1)

ρ : density of the solid phase in the freshwater compartment of zone *z* [$kg_{solid\ phase}$ per $m^3_{solid\ phase}$] (defined as described in section B.5.4).

The k-value is representative only for one type of freshwater fish. If there are different types of freshwater fish caught in one freshwater compartment and if any of the parameters 'production rate' or 'BCF' differs, a sum over the respectively resulting k-values needs to be computed according to (for the explanation of the symbols refer to the equation above):

$$k_{w,\ uptake+catch\ fish} = \frac{1}{Ksw \cdot ED_{bulk/solid} \cdot \rho_{suspendend\ matter}(w,z)} \cdot \sum_{x\ \cdot\ r_1, r_2, \ldots} \{BCF\_V/fw_{fish/water}(p,r,e) \cdot P(r,n)\} \quad \text{(A-33)}$$

Note that the production rate needs to be distributed from administrative units (denoted by *n* here) to zones. This is done on an area-weighted basis.

A.3.9 Discharge

Discharge or rate of flow is defined as "volume of water flowing through a river (or channel) cross section in unit time" (Deutsches Nationalkomitee für das internationale Hydrologische Programm (IHP) der UNESCO und das Operationelle Hydrologische Programm (OHP) der WMO, 1998, p. 45). It is simply modelled by employing the value for discharge:

$$k_{w,\ z1-z2,\ discharge}(z) = Q_{discharge}(z) \quad \text{(A-34)}$$

where

k : process rate for discharge [m^3 per s]

Q : discharge occurring in zone z [m^3 per s] (defined in section B.5.2).

A.3.10 Water circulation in large lakes

In section B.2.1, reasons are given why some larger lakes are distinguished as separate zones. Following the Pfafstetter code system (section 4.3), only cascade-like downstream orientated flows can be determined. Due to the rather unnatural herringbone-like differentiation of larger lakes (cf. Fig. 6-2), the additional process 'water circulation in large lakes' has been introduced in order to also allow for an 'upstream' flow between zones of larger lakes. It is formulated analogously to the downstream flow process 'discharge' (section A.3.9) while adding the factor fr_Q:

$$k_{w,\, z_{down} - z_{up,i},\, \text{lake ciculation}}(z, w) = Q_{\text{discharge}}(z_{down}, w) \cdot fr\_Q_{\text{lake circulation}}(w) \qquad \text{(A-35)}$$

where

k : process rate for water circulation in large lakes [m^3 per s]

fr_Q : fraction of the discharge flowing out of zone z_{down} that is allowed to undergo 'upstream' flow into zone $z_{up,i}$ where the count of i may range from 0 to 2 depending on how many 'upstream' lake zones exist [-]; set to unity

Q : discharge occurring in zone z_{down} [m^3 per s] (defined in section B.5.2).

In order for the water mass balance to result, the same amount of water is set to flow from the potentially two upstream lake zones $z_{up,i}$ into the one downstream z_{down} according to:

$$k_{w,\, z_{up,i} - z_{down},\, \text{lake ciculation}}(z, w) = Q_{\text{discharge}}(z_{down}, w) \cdot fr\_Q_{\text{lake circulation}}(w)\,. \qquad \text{(A-36)}$$

A.3.11 Sedimentation (or sediment deposition) in freshwater compartments

Sedimentation is defined as the "(p)rocess of settling and depositing by gravity of suspended matter in water" (Deutsches Nationalkomitee für das internationale Hydrologische Programm (IHP) der UNESCO und das Operationelle Hydrologische Programm (OHP) der WMO, 1998, p. 133). It is, thus, a process involved in the particle mass turn-over in an aquatic ecosystem.

As discussed in sections 6.1, B.4 and B.5.4, the behaviour of streams is treated differently from that of large lakes. The overall process of sediment deposition is calculated according to:

$$k_{w\text{-}ws,\ \text{sedimentation, pH|pH inv|C}_{org}}(p, w, z) = \frac{A(z) \cdot fr\_A(w, z)}{ED_{\text{bulk aqueous, pH|pH inv|C}_{org}}(p, w, z) \cdot [v_{\text{sedimentation, lake}}(w) \cdot fr\_V_{\text{stagnant}}(w, z) + v_{\text{sedimentation, stream}}(w) \cdot (1 - fr\_V_{\text{stagnant}}(w, z))]} \quad \text{(A-37)}$$

where

A : area of zone z [m^2] (defined in section B.2)

ED : equilibrium distribution coefficient of a substance p of the respective compartment i of zone z that may depend on a compartment's pH or organic carbon content [-] (defined in section A.2)

fr_A : area fraction of the freshwater compartment in zone z [-] (defined in section B.3)

fr_V : volume fraction of the freshwater compartment in zone z that is stagnant water [-] (defined in section B.5.4)

k : process rate for sedimentation [m^3 per s]

v : suspended matter deposition velocity in stagnant or flowing waters [m per s] (defined in section B.5.4).

For evaluative purposes, an additional formulation is implemented in WATSON which is in line with state-of-the-art multimedia models and does not take into account the weighting by the stagnant water volume. Instead an overall sedimentation rate is assumed for all water bodies. The rate corresponds to the pure lake condition as given in Table 6-4.

A.3.12 Resuspension of bottom sediment matter

Resuspension may be defined as the process that causes solids in the bottom sediment of a water body to become suspended again in the water column. Thus, resuspension is a process involved in the particle mass turn-over in an aquatic ecosystem. It is, therefore, mostly concerned with the translocation of particles. In most of the multimedia models which focus on the fate of lipophilic organic compounds which are hardly encountered in solution, it is reasonable to concentrate on the fraction of the substances that are bound to particles. However, particles are set into motion by eddies or currents in the water which will also entrain the surrounding aqueous phase of the sediments. This is especially important for more hydrophilic compounds like several metals and their compounds. As a result, the process 'resuspension' is considered here to not only set a part of the sediment compartment into motion so that the sediment particles become suspended again but also to drag along the sediment pore water formerly surrounding those re-suspended particles. The rate is assumed to be the same for both of these phases. Thus, no equilibrium distribution coefficient is considered in Eq. (A-38) describing this process.

As discussed in sections 6.1, B.4 and B.5.4, the behaviour of streams is treated differently from that of large lakes. The overall process of resuspension is calculated according to:

$$k_{ws\text{-}w,\,\text{resuspension}}(ws, z) = \mathrm{A}(z) \cdot fr\_A(w, z) \cdot [v_{\text{resuspension, lake}}(ws) \cdot fr\_\mathrm{A}_{\text{stagnant water}}(ws, z) + v_{\text{resuspension, stream}}(ws) \cdot (1 - fr\_\mathrm{A}_{\text{stagnant water}}(ws, z))] \quad \text{(A-38)}$$

where

A : area of zone z [m^2] (defined in section B.2)

fr_A : fr_A: area fraction of the freshwater compartment in zone z [-] (defined in section B.3)

$fr\_A_{stagnant}$: area fraction of the freshwater sediment compartment in zone z that is located below stagnant water [-] (defined in section B.5.4)

k : process rate for resuspension [m^3 per s]

v : resuspension velocity in stagnant or flowing waters [m per s] (defined in section B.5.4).

For evaluative purposes, an additional formulation is implemented in WATSON which is in line with state-of-the-art multimedia models. It reads for pH-dependent partitioning:

$$k_{ws\text{-}w,\ \text{resuspension},\ \text{pH}}(ws, z) = \mathrm{A}(z) \cdot fr\_A(w, z) \cdot v_{\text{sedimentation}}(w) \cdot fr\_v_{\text{resuspended sedimentation}}(ws) \cdot \frac{Ksw(p, pH(z, ws)) \cdot \rho_{\text{solid phase}}(ws, z)}{ED_{\text{bulk aqueous, pH}}(p, ws, z)} \quad \text{(A-39)}$$

and for organic carbon-dependent partitioning:

$$k_{ws\text{-}w,\ \text{resuspension},\ \text{Corg}}(ws, z) = \mathrm{A}(z) \cdot fr\_A(w, z) \cdot v_{\text{sedimentation}}(w) \cdot fr\_v_{\text{resuspended sedimentation}}(ws) \cdot \frac{Ksw_{C_{org}}(p, ws, z) \cdot \rho_{\text{solid phase}}(ws, z)}{ED_{\text{bulk aqueous, } C_{org}}(p, ws, z)} \quad \text{(A-40)}$$

where

A : area of zone z [m^2] (defined in section B.2)

ED : equilibrium distribution coefficient of a substance p of the sediment compartment of zone z relating the bulk concentration to the aqueous phase concentration [-] (defined in section A.2)

fr_A : area fraction of the freshwater compartment in zone z [-] (defined in section B.3)

fr_v : fraction of sedimentation rate being resuspended [-] (defined as described in Table 6-4 for pure lake conditions)

K_{sw} : solid-water partitioning coefficient of substance p that may depend on organic carbon or pH [$m^3_{\text{aqueous phase}}$ per $kg_{\text{solid phase}}$] (defined in section C.1.1)

k : process rate for resuspension [m^3 per s]

ρ : density of the solid phase [$kg_{\text{solid phase}}$ per $m^3_{\text{solid phase}}$] (defined as described in section B.5.4)

v : sedimentation velocity [m per s] (defined as described in Table 6-4 for pure lake conditions).

A.3.13 Sediment burial

Burial refers to the rate at which contaminants move from the active to the inactive sediment layer. In contrast to resuspension in which both the solid and the aqueous phase are involved, only the particles are assumed to undergo this process. This is because the volume fraction of water decreases substantially with sediment depth so that the water is thought to 'stay' whereas the solids settle and become compacted.

As discussed in sections 6.1, B.4 and B.5.4, the behaviour of streams is treated differently from that of large lakes. The overall process of sediment burial for substances whose partitioning behaviour is dependent on the sediment's pH is calculated according to:

$$k_{ws,\,\text{burial},\,\text{pH|pH}_{inv}}(p, ws, z) = \mathrm{A}(z) \cdot fr\_A(w, z) \cdot \frac{\rho_{\text{solid phase}}(ws, z) \cdot Ksw(p, pH(ws, z))}{ED_{\text{bulk/aqueous},\,\text{pH|pH}_{inv}}(p, ws, z)} \cdot [v_{\text{burial, lake}}(ws) \cdot fr\_\mathrm{A}_{\text{stagnant water}}(ws, z) + v_{\text{burial, stream}}(ws) \cdot (1 - fr\_\mathrm{A}_{\text{stagnant water}}(ws, z))] \quad \text{(A-41)}$$

For partitioning dependent on the sediment's organic carbon content, the calculation reads:

$$k_{ws,\,\text{burial},\,\mathrm{C_{org}}}(p, ws, z) = \mathrm{A}(z) \cdot fr\_A(w, z) \cdot \frac{\rho_{\text{solid phase}}(ws, z) \cdot Ksw_{\mathrm{C_{org}}}(p, ws, z)}{ED_{\text{bulk/aqueous},\,\mathrm{C_{org}}}(p, ws, z)} \cdot [v_{\text{burial, lake}}(ws) \cdot fr\_\mathrm{A}_{\text{stagnant water}}(ws, z) + v_{\text{burial, stream}}(ws) \cdot (1 - fr\_\mathrm{A}_{\text{stagnant water}}(ws, z))] \quad \text{(A-42)}$$

where

A : area of zone z [m^2] (defined in section B.2)

ED : equilibrium distribution coefficient of a substance p of the respective compartment i of zone z relating the bulk concentration to the aqueous phase concentration [-] (defined in section A.2)

fr_A : fr_A: area fraction of the freshwater compartment in zone z [-] (defined in section B.3)

$fr\_A_{stagnant}$: area fraction of the freshwater sediment compartment in zone z that is located below stagnant water [-] (defined in section B.5.4)

K_{sw} : solid-water partitioning coefficient of substance p that may depend on organic carbon or pH [$m^3_{aqueous\ phase}$ per $kg_{solid\ phase}$] (defined in section C.1.1)

k : process rate for sediment burial [m^3 per s]

ρ : density of the solid phase [$kg_{solid\ phase}$ per $m^3_{solid\ phase}$] (defined as described in section B.5.4)

v : sediment burial velocity in stagnant or flowing waters [m per s] (defined in section B.5.4).

For evaluative purposes, an additional formulation is implemented in WATSON which is in line with state-of-the-art multimedia models. It reads for pH-dependent partitioning:

$$k_{ws,\,burial,\,pH}(p, ws, z) = A(z) \cdot fr\_A(w, z) \cdot v_{sedimentation}(w) \cdot fr\_v_{burial/sedimentation}(ws) \cdot \frac{Ksw(p, pH(z, ws)) \cdot \rho_{solid\ phase}(ws, z)}{ED_{bulk\ aqueous,\,pH}(p, ws, z)} \quad \text{(A-43)}$$

and for organic carbon-dependent partitioning:

$$k_{ws,\,burial,\,C_{org}}(p, ws, z) = A(z) \cdot fr\_A(w, z) \cdot v_{sedimentation}(w) \cdot fr\_v_{burial/sedimentation}(ws) \cdot \frac{Ksw_{C_{org}}(p, ws, z) \cdot \rho_{solid\ phase}(ws, z)}{ED_{bulk/aqueous,\,C_{org}}(p, ws, z)} \quad \text{(A-44)}$$

where

A : area of zone z [m^2] (defined in section B.2)

ED : equilibrium distribution coefficient of a substance p of the respective compartment i of zone z relating the bulk concentration to the aqueous phase concentration [-] (defined in section A.2)

fr_A : area fraction of the freshwater compartment in zone z [-] (defined in section B.3)

fr_v : fraction of sedimentation rate finally buried [-] (defined as described in Table 6-4 for pure lake conditions)

K_{sw} : solid-water partitioning coefficient of substance p that may depend on organic carbon or pH [$m^3_{aqueous\ phase}$ per $kg_{solid\ phase}$] (defined in section C.1.1)

k : process rate for resuspension [m^3 per s]

ρ : density of the solid phase [$kg_{solid\ phase}$ per $m^3_{solid\ phase}$] (defined as described in section B.5.4)

v : sedimentation velocity [m per s] (defined as described in Table 6-4 for pure lake conditions).

A.3.14 Diffusion from water body to sediment

Apart from advective processes, substances may also migrate from one compartment into another due to diffusion. This migration is usually described based on the stagnant two-film model or two-resistance theory (Mackay, 1985; Schwarzenbach et al., 1993; Cowan et al., 1995b; Brandes et al., 1996; Wania et al., 2000). The inverse of the mass transfer coefficients or velocities can be interpreted as a transfer resistance. This also applies to diffusion taking place at the sediment-water interface. In contrast to the soil-air interface, there are only two resistances which are connected in series. The overall mass transfer coefficients $v_{diffusion}$ results accordingly:

$$\frac{1}{v_{diffusion}} = \frac{1}{v_{diffusion,\ sediment\text{-}side}} + \frac{1}{v_{diffusion,\ water\text{-}side}} \qquad \text{(A-45)}$$

$$\Rightarrow v_{diffusion} = \frac{v_{diffusion,\ sediment\text{-}side} \cdot v_{diffusion,\ water\text{-}side}}{v_{diffusion,\ sediment\text{-}side} + v_{diffusion,\ water\text{-}side}}$$

The respective sediment-side and water-side partial mass transfer coefficients can generally be computed by dividing the respective effective diffusivities by their corresponding diffusion path lengths (Schwarzenbach et al., 1993). However, a generic value for the overall mass transfer coefficient will be employed here (see section B.4.4).

The overall process of diffusion from water body into sediment for substances whose partitioning behaviour is dependent on the sediment's pH is calculated according to:

$$k_{w\text{-}ws,\,\mathrm{diffusion},\,\mathrm{pH|pH_{inv}}}(p, w, z) = (\mathrm{A}(z) \cdot fr\_A(w, z) \cdot v_{\mathrm{diffusion}}(w))/ [ED_{\mathrm{bulk/solid},\,\mathrm{pH|pH_{inv}}}(p, w, z) \cdot Ksw(p, pH(w, z)|pH(w)) \cdot \rho_{\mathrm{suspended\ matter}}(w, z)] \quad \text{(A-46)}$$

For partitioning dependent on the sediment's organic carbon content, the calculation reads:

$$k_{w\text{-}ws,\,\mathrm{diffusion},\,\mathrm{C_{org}}}(p, w, z) = (\mathrm{A}(z) \cdot fr\_A(w, z) \cdot v_{\mathrm{diffusion}}(w))/ [ED_{\mathrm{bulk/solid},\,\mathrm{C_{org}}}(p, w, z) \cdot Ksw_{\mathrm{C_{org}}}(p, w, z) \cdot \rho_{\mathrm{suspended\ matter}}(w, z)] \quad \text{(A-47)}$$

where

A : area of zone z [m^2] (defined in section B.2)

ED : equilibrium distribution coefficient of a substance p of the respective compartment i of zone z relating the bulk concentration to the solid phase concentration [-] (defined in section A.2)

fr_A : area fraction of the freshwater compartment in zone z [-] (defined in section B.3)

K_{sw} : solid-water partitioning coefficient of substance p that may depend on organic carbon or pH [$m^3_{\mathrm{aqueous\ phase}}$ per $kg_{\mathrm{solid\ phase}}$] (defined in section C.1.1)

k : process rate for diffusion from water body into sediment [m^3 per s]

ρ : density of the solid phase in the freshwater compartment of zone z [$kg_{\mathrm{solid\ phase}}$ per $m^3_{\mathrm{solid\ phase}}$] (defined as described in section B.5.4)

v : overall mass transfer coefficient for diffusion at the sediment-water interface [m per s] (defined in section B.4.4).

Note that the denominator corresponds to the equilibrium distribution coefficient that relates the bulk concentration to the aqueous phase concentration in the water compartment (cf. Eq. (A-18)).

A.3.15 Diffusion from sediment to water body

The process 'diffusion from sediment to water body' is described in analogy to that of the reverse process presented in section A.3.14 where also a discussion on the overall mass transfer coefficient is provided:

$$k_{ws\text{-}w,\,\text{diffusion, pH|pH inv|C}_{org}}(p, ws, z) = A(z) \cdot fr\_A(w, z) \cdot \frac{v_{\text{diffusion}}(ws)}{ED_{\text{bulk/aqueous, pH|pH inv|C}_{org}}(p, ws, z)} \quad \text{(A-48)}$$

where

A : area of zone z [m^2] (defined in section B.2)

ED : equilibrium distribution coefficient of a substance p of the respective compartment i of zone z relating the bulk concentration to the aqueous phase concentration [-] (defined in section A.2)

fr_A : area fraction of the freshwater compartment in zone z [-] (defined in section B.3)

k : process rate for diffusion from water body into sediment [m^3 per s]

v : overall mass transfer coefficient for diffusion at the sediment-water interface [m per s] (defined in section B.4.4).

A.4 Volume calculations

In order to compute the dynamic solution (cf. section A.1), it is necessary to know the volumes of each of the compartments. Three different equations are employed taking account of the different ways the volumes are determined:

1. terrestrial compartments other than impervious surfaces are assumed to have an invariant depth throughout the entire model's scope (cf. section 5.1.2),
2. impervious surfaces such as pavements are by definition impervious and do, thus, not have a real depth. On the other hand, they are not expected to constitute compartments that show long retention times. Therefore, their volume is set to the total annual amount of precipitation occurring at a given site (cf. section 5.1.10), and
3. the freshwater compartments have variable volumes depending on whether large lakes are present in a zone and also depending on the location within a

larger catchment (freshwater volume increases towards the river mouth, cf. section B.4). The volumes are at present determined externally and are directly provided. The same applies to freshwater sediments although having a constant depth.

The determination of the volumes is described in the following.

A.4.1 Volume calculation: non-urban terrestrial compartments

Volumes of terrestrial compartments with constant depths, i.e., arable land (*i*: ag), pastures (*i*: p), semi-natural ecosystems (*i*: n), non-vegetated land (*i*: b), glaciers (*i*: gl), are calculated according to:

$$V(i,z) = \mathrm{A}(z) \cdot fr\_A(i,z) \cdot d(i) \qquad \text{(A-49)}$$

where

A : area of zone z [m^2] (defined in section B.2)

fr_A : area fraction of compartment i in zone z [-] (defined in section B.3)

d : depth of compartment i [m] (defined in section 5.1)

V : volume of compartment i in zone z [m^3].

A.4.2 Volume calculation: urban/built-up area

The depth of the impervious compartment varies between zones (cf. section 5.1.10). The volume is calculated according to:

$$V(u,z) = \mathrm{A}(z) \cdot fr\_A(u,z) \cdot d(u,z) \qquad \text{(A-50)}$$

where

A : area of zone z [m^2] (defined in section B.2)

fr_A : area fraction of the impervious land compartment in zone z [-] (defined in section B.3)

d : depth of the impervious land compartment [m] (defined in section 5.1.10)

V : volume of the impervious land compartment in zone z [m^3].

A.4.3 Volume calculation: water and sediment

The volumes of the freshwater (*i*: w) and sediment compartments (*i*: ws) are calculated externally and provided in the database. The volume calculation simplifies to:

$$V(i,z) = V(i,z) \tag{A-51}$$

where

V : volume of compartment *i* in zone *z* [m^3].

A.5 Background concentration calculation

When calculating dynamically in the followed mathematical approach (cf. Eq. (A-1)), an initial concentration needs to be specified. If a 'pristine' environment is assumed, these background concentrations are set to zero. However, if emission takes places into an environment in which appreciable substance amounts are already present, it can be set to non-zero values for any compartment *i* distinguished:

$$\begin{aligned} bg_{\text{zero}}(i,z) &= 0 && \text{when no background is assumed} \\ bg_{\text{non-zero}}(p,i,z) &= C\_w/v_{\text{background}}(p,i) && \text{when background is considered} \end{aligned} \tag{A-52}$$

where

bg : background concentration of substance *p* in compartment *i* of zone *z* [kg per m^3]

C_w/v : background concentration of substance *p* in compartment *i* [kg per m^3].

Note that the non-zero background concentrations are at present only allowed to vary by compartments and not by zones.

A.6 Exogenous input formulations

Any model that is confined to a part of a system that is not entirely closed needs to set boundary conditions. According to the followed mathematical approach, the boundary conditions consist of the perturbation vector ($\vec{b}$ in Eq. (A-1)) that defines exogenous inputs into the modelled system. Results from air quality models or releases directly into the media soil or water may constitute such exogenous inputs. The way these are formulated is described in the following sections.

A.6.1 Direct emissions into soil or water

Direct emissions may principally occur into any compartment distinguished although substantial releases of substances directly into sediments or glaciers are rather unlikely to occur. At present only releases into arable land (*i*: ag) and freshwater (*i*: w) are distinguished which may be due to soil amendments or sewer effluents for instance (note that similar to the exposure assessment the specification of direct releases into water and soil is according to administrative units, cf. Fig. B-4):

$$S_{j,\,\text{direct input}}(s, p, i, z) = S(s, p, i, z) \qquad \text{(A-53)}$$

where

S : source strength of substance *p* into compartment *i* of zone *z* according to scenario *s* due to direct releases [kg per s].

A.6.2 Atmospheric deposition - wet

Atmospheric deposition is usually distinguished into wet and dry (e.g., Seinfeld, 1986). During wet atmospheric deposition, substances in air are absorbed by droplets which in turn are removed from the atmosphere by precipitation. Any compartment in contact with the atmosphere, i.e., arable land (*i*: ag), pastures (*i*: p), semi-natural ecosystems (*i*: n), non-vegetated land (*i*: b), glaciers (*i*: gl), impervious surfaces (*i*: u) and freshwater (*i*: w), may receive inputs by this process:

$$S_{a\text{-}i,\,\text{wet atmospheric deposition}}(z, s, p, i) = A(z) \cdot fr\_\mathrm{A}(i, z) \cdot ATMDEP_{\text{wet}}(s, p, z) \qquad \text{(A-54)}$$

where

A : area of zone *z* [m^2] (defined in section B.2)

ATMDEP : wet atmospheric deposition of substance *p* in zone *z* for scenario *s* [kg per m^2 per s][40]

fr_A : area fraction of compartment *i* in zone *z* [-] (defined in section B.3)

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[40] Note that the atmospheric deposition may stem from different sources. These may be reported depositions or those estimated by means of air quality models. Presently, the results from the Windrose Trajectory Model (WTM) as described in section 4.1 are used.

S : source strength of substance p into compartment i of zone z according to scenario s due to wet atmospheric deposition [kg per s].

A.6.3 Atmospheric deposition - dry

Atmospheric deposition is usually distinguished into wet and dry (e.g., Seinfeld, 1986). During dry atmospheric deposition, substances in air are taken up by the earth's surface which may constitute of soil, water, or vegetation. Any compartment in contact with the atmosphere, i.e., arable land (i: ag), pastures (i: p), semi-natural ecosystems (i: n), non-vegetated land (i: b), glaciers (i: gl), impervious surfaces (i: u) and freshwater (i: w), may receive inputs by this process:

$$S_{a\text{-}i,\ \text{dry atmospheric deposition}}(z, s, p, i) = A(z) \cdot fr\_\mathrm{A}(i, z) \cdot ATMDEP_{\text{dry}}(s, p, z) \qquad \text{(A-55)}$$

where

A : area of zone z [m^2] (defined in section B.2)

ATMDEP : dry atmospheric deposition of substance p in zone z for scenario s [kg per m^2 per s][40]

fr_A : area fraction of compartment i in zone z [-] (defined in section B.3)

S : source strength of substance p into compartment i of zone z according to scenario s due to dry atmospheric deposition [kg per s].

A.6.4 Wet atmospheric deposition considering preferential flow/ leaching

When considering preferential flow which is discussed in section A.3.7, the wet atmospheric deposition needs to be treated differently from what was presented in section A.6.2. In general, one needs to distinguish permeable from impermeable surfaces. This is because the process formulation for impermeable compartments follows that of the 'ordinary' case.

Wet atmospheric deposition to permeable soils (preferential flow distinguished)

When allowing preferential flow to be active (cf. section A.3.7), it is assumed that a certain fraction of the precipitation instantly passes the top soil which is represented by the soil compartment (cf. section 5.1.2). Thus, this portion of the precipitation and the corresponding substances contained therein are directly moved to below the top soil. As a result, this portion of the wet atmospheric deposition needs to be disregarded in terms of input to the top soil. The process affects any compartment that may receive inputs from the atmosphere and is permeable, i.e., arable land (*i*: ag), pastures (*i*: p), semi-natural ecosystems (*i*: n) and non-vegetated land (*i*: b):

$$S_{a\text{-}i,\ \text{wet atmospheric deposition/pref flow}}(z, s, p, i) = A(z) \cdot fr\_\mathrm{A}(i, z) \cdot ATMDEP_{\text{wet}}(s, p, z) \cdot (1 - fr\_v_{\text{pref flow/rain}}(z)) \quad \text{(A-56)}$$

where

A : area of zone z [m^2] (defined in section B.2)

ATMDEP : wet atmospheric deposition of substance p in zone z for scenario s [kg per m^2 per s][40]

fr_A : area fraction of compartment i in zone z [-] (defined in section B.3)

fr_V : fraction of precipitation undergoing preferential flow in zone z [-] (defined in section B.5.2)

S : source strength of substance p into compartment i of zone z according to scenario s due to wet atmospheric deposition allowing for preferential flow [kg per s].

Wet atmospheric deposition to compartments other than permeable soils (preferential flow distinguished)

The process formulation for impermeable compartments including freshwater follows that as presented in section A.6.2. The only difference that exists concerns the compartments to which it applies. These are freshwater (*i*: w), glacier (*i*: gl) and urban/built-up area/impervious surface (*i*: u).

Wet atmospheric deposition to the subsurface through preferential flow/leaching

If the subsurface of the top soil was distinguished (e.g., ground water), the direct input from the atmosphere to this part of the environment via preferential flow would need to be described explicitly. Preferential flow can of course only occur if the ground that receives atmospheric inputs is permeable at all, i.e., covered by the compartments arable land (*i*: ag), pastures (*i*: p), semi-natural ecosystems (*i*: n) and non-vegetated land (*i*: b). In order to define the permeable share of the zonal area, the area shares of freshwater (*i*: w), glacier (*i*: gl) and urban/built-up area/impervious surface (*i*: u) are subtracted from the total area share of 100 % if these compartments exist:

$$S_{a\text{-}j,\,\text{wet atmospheric deposition}}(z,s,p) = A(z)\cdot fr\_v_{\text{pref flow/rain}}(z)\cdot (1-fr\_A(w,z)-fr\_A(gl,z)-fr\_A(u,z))\cdot ATMDEP_{\text{wet}}(s,p,z) \quad \text{(A-57)}$$

where

A : area of zone z [m^2] (defined in section B.2)

ATMDEP : wet atmospheric deposition of substance p in zone z for scenario s [kg per m^2 per s][40]

fr_A : area fraction of the compartments freshwater (*i*: w), glacier (*i*: gl) and/or urban/built-up area/impervious surface (*i*: u) in zone z [-] (defined in section B.3)

fr_V : fraction of precipitation undergoing preferential flow in zone z [-] (defined in section B.5.2)

S : source strength of substance p into compartment j of zone z according to scenario s due to preferential flow [kg per s].

A.6.5 Removal of atmospheric deposition due to harvest of exposed aboveground produce

In general, aboveground plant parts intercept a portion of the dry and wet atmospheric deposition. In the case of exposed aboveground produce, i.e., produce that is in direct contact with the atmosphere, the intercepted portion of the substance may contribute directly or indirectly to human exposure. In order to allow for removal of substances which are intercepted due to harvest, two process formulations are suggested here.

Table A-1: Parameter needs for the assessment of particle deposition to aboveground produce that are neither related to substance nor to plant characteristics (like plant biomass, time until harvest)

Reference	Parameter required	Remarks
TRIM.FaTE (United States - Environmental Protection Agency, 2002b)	Interception fraction for dry deposition [-]	used in equations TF 7-1 and TF 7-2 (ibid.); can be derived if vegetation attenuation factor [m^2/kg], wet aboveground non-woody vegetation biomass inventory per unit area [kg/m^2] and water content of leaves [-] are known
	Interception fraction for wet deposition [-]	used in equations TF 7-3 and TF 7-4a (ibid.); can be derived by the LAI [-], vegetation-dependent leaf-wetting factor [m] and amount of rainfall of a rainfall event [m] are known or use the default value of 0.2
Equation 5-13 in (United States - Environmental Protection Agency, 1998)	Fraction of wet deposition that adheres to plant surfaces [-]	recommended value (Table B-2-7, ibid.): 0.2 for anions 0.6 for cations and organics and insoluble particles
	Interception fraction of the edible portion of plant tissue [-]	can either be derived with the help of an empirical constant and the standing crop biomass [kg/m^2] or a recommended value can be used which is 0.39 (see section 5.3.1.1, ibid.)
	Plant surface loss coefficient [$time^{-1}$]	recommended value (section 5.3.1.2, ibid.): 18 [$year^{-1}$] ~ 0.05 [day^{-1}]; the parameter allows for wind removal, water removal and growth dilution and is stated to be conservative as it does not include degradation

There are only two models given in Table 5-8 describing particulate deposition to plant surfaces (United States - Environmental Protection Agency, 1998, 2002b). Both methods are fairly data-intensive, requiring data for the parameters described in Table A-1 that are neither related to substance nor to plant characteristics (like plant biomass, time until harvest).

A closer look at the definition of the parameters in Table A-1 reveals that the parameter 'Interception fraction of the edible portion of plant tissue' and 'Interception fraction for dry deposition' are identical (defined by the same formula of the same reference). The recommended value for 'Interception fraction of the edible portion of plant tissue' in United States - Environmental Protection Agency (1998) could, thus, also be used as a default value for 'Interception fraction for dry deposition' used by TRIM.FaTE (United States - Environmental Protection Agency, 2002b).

It appears that there are two options for the inclusion of the particulate deposition process for non-volatile substances:

1. relying on net adsorption rates as provided by United States - Environmental Protection Agency (1998) which can be combined with a harvest rate without distinguishing a separate 'particles on plant/leaves' compartment or
2. modelling deposition and additionally removal either due to blow off or wash off in the environmental fate model according to TRIM.FaTE (United States - Environmental Protection Agency, 2002b) by introducing a separate 'particles on plant/leaves' compartment.

In either case, the use of quite a few default values seems to be necessary. Also it must be taken account of the fact that the soil below the vegetation compartment receives less input directly from air.

The net adsorption approach under number 1) is adopted for the following reasons. In TRIM.FaTE the processes wash off and blow off of particles from leaves only occur when there is or there is no rain, respectively. This would bring about the need to distinguish between rain and non-rain episodes being accomplished by a meteorological (on/off) toggle in TRIM.FaTE which is not available in the air quality model WTM (described in section 4.1) based on which the present environmental fate and exposure assessment is performed. A second reason is that it is tried here not to introduce too many compartments into the environmental fate model. A third reason might be that the formulation of exchange processes with the plant interior poses difficulties (Riederer, 1995; and note in Maddalena et al., 2002) although these are not so much relevant for non-volatile metals for which the question whether these penetrate the plant cuticle or not is unresolved (see section 5.2.1).

United States - Environmental Protection Agency (1998) recommends equation 5-14 (given therein) for the assessment of concentrations in exposed aboveground produce. This equation relates emissions to plant concentrations. However, interception concerns depositions of particles or droplets which is why equation 5-13 (ibid.) relating depositions to plant concentrations is made use of here. This also complies to the mathematical formulation of multimedia models in general and WATSON specifically.

The Leaf Area Index (LAI) is implicitly taken into account by the two correction factors for the adhering fraction of wet deposition and the interception fraction of edible parts. In the '1 minus exponent' term the time duration of the actual exposure of the edible parts needs to be specified. Unlike for leafy produce, the exposure time of fruits that only appear after impregnation of the blossom will be shorter than the full growing season of the respective plant. Fruits are not explicitly mentioned here but can be treated equivalently.

Removal processes need to be formulated for dry and wet atmospheric deposition separately in order to allow for subtraction from the respective 'pure' atmospheric deposition process. Note that this process is not formulated for forage taken in for example by cattle. This is mainly because there is no statistical production data available in the FAO statistical database presumably due to the fact that forage is not traded (across national borders).

Removal from dry atmospheric deposition due to harvest of exposed aboveground produce

The removal from the dry atmospheric deposition is formulated as:

$$S_{\text{a-ag, dry deposition+harvest exposed crops}} = -ATMDEP_{\text{dry}}(s,p,z) \cdot emp_{\text{plant surface loss}}(r,e) \cdot fr\_w_{\text{intercept/deposition}}(r,e) \cdot \frac{P(r,n)}{Y\_fw(r,n,e)} \quad \text{(A-58)}$$

where

ATMDEP : dry atmospheric deposition of substance p in zone z for scenario s [kg per m^2 per s][40]

emp : empirical correction factor for physical surface loss from plant r [s] (defined below)

fr_w : mass fraction of a substance that is intercepted by aboveground exposed produce r during atmospheric deposition [kg per kg]; 0.39 (United States - Environmental Protection Agency, 1998, p. 5-28)

P : annual production rate of crop r in administrative unit n [kg FW per s] (defined as described in section B.6.1)

S : source of substances [kg per s]; note that this is negative here as this part of the atmospheric deposition is directly redirected into the exposure assessment

Y_fw : yield of aboveground exposed produce r in administrative unit n [kg FW per m^2] (defined as described in section B.6.1).

The empirical correction factor is pre-calculated according to:

$$emp_{\text{plant surface loss}}(r, e) = \frac{1 - 10^{-(r_{\text{plant surface loss}}(r, e) \cdot t_{\text{exposure duration}}(r, e))}}{r_{\text{plant surface loss}}(r, e)} \quad \text{(A-59)}$$

where

emp : Empirical correction factor for physical surface loss from plant r [s]

r : Physical surface loss rate for plant r [per s]; $5.7 \cdot 10^{-7}$ (United States - Environmental Protection Agency, 1998, p. 5-29)

t : Exposure duration of exposed produce r [s]; 5184000 (United States - Environmental Protection Agency, 1998, p. 5-30).

The S-value is representative only for one type of crop. If there are different types of aboveground exposed crops produced on one agricultural soil compartment and if any of the parameters 'production rate', 'yield of aboveground exposed produce', 'mass fraction of a substance that is intercepted', or 'empirical correction factor' differs, a sum over the respectively resulting S-values needs to be computed according to (for the explanation of the symbols refer to Eq. (A-58)):

$$\begin{aligned} S_{\text{a, dry deposition+harvest exposed crops}} = {} & -ATMDEP_{\text{dry}}(s, p, z) \cdot \\ & emp_{\text{plant surface loss}}(r, e) \cdot \\ & \sum_{x = r_1, r_2, \ldots} \left[fr\_w_{\text{intercept/deposition}}(x, e) \cdot \right. \\ & \left. \frac{P(x, n)}{Y\_fw(x, n, e)} \right] \end{aligned} \quad \text{(A-60)}$$

Note that the empirical factor at present does not distinguish between different aboveground exposed crops and is, therefore, not contained in the sum. Further note that the production rate needs to be distributed from administrative units to zones, denoted by n and z respectively (cf. sections B.6 and B.2 on the respective spatial differentiation). This is done on an area-weighted basis.

Removal from wet atmospheric deposition due to harvest of exposed aboveground produce

The removal from wet atmospheric deposition due to harvest of exposed aboveground produce is formulated as:

$$S_{\text{a-ag, wet deposition+harvest exposed crops}} = -ATMDEP_{\text{wet}}(s,p,z) \cdot fr\_w_{\text{adhere wet deposition}}(p,r,e) \cdot emp_{\text{plant surface loss}}(r,e) \cdot fr\_w_{\text{intercept deposition}}(r,e) \cdot \frac{P(r,n)}{Y\_fw(r,n,e)} \quad \text{(A-61)}$$

where

ATMDEP : dry atmospheric deposition of substance p in zone z for scenario s [kg per m^2 per s][40]

emp : empirical correction factor for physical surface loss from plant r [s] (for its computation see above)

fr_w : $\text{fr\_w}_{\text{adhere/wet deposition}}$: mass fraction of a substance's p wet deposition that adheres to aboveground exposed produce r [kg per kg] (defined in Table C-7)

$\text{fr\_w}_{\text{intercept/deposition}}$: mass fraction of a substance that is intercepted by aboveground exposed produce r during atmospheric deposition [kg per kg]; 0.39 (United States - Environmental Protection Agency, 1998, p. 5-28)

P : annual production rate of crop r in administrative unit n [kg FW per s] (defined as described in section B.6.1)

S : source of substances [kg per s]; note that this is negative here as this part of the atmospheric deposition is directly redirected into the exposure assessment

Y_fw : yield of aboveground exposed produce r in administrative unit n [kg FW per m^2] (defined as described in section B.6.1).

The S-value is representative only for one type of crop. If there are different types of aboveground exposed crops produced on one agricultural soil compartment and if any of the parameters 'production rate', 'yield of aboveground exposed produce', 'mass fraction of a substance that is intercepted', 'mass fraction

of a substance's wet deposition that adheres to aboveground exposed produce', or 'empirical correction factor' differs a sum over the respectively resulting S-values needs to be computed according to (for the explanation of the symbols refer to the equation above):

$$S_{\text{a, wet deposition+harvest exposed crops}} = -ATMDEP_{\text{wet}}(s, p, z) \cdot emp_{\text{plant surface loss}}(r, e) \cdot \sum_{x = r_1, r_2, \ldots} \left[\frac{P(x, n)}{Y\_fw(x, n, e)} \cdot fr\_w_{\text{intercept/deposition}}(x, e) \cdot fr\_w_{\text{adhere/wet deposition}}(p, x, e) \right] \quad \text{(A-62)}$$

Note that the empirical factor at present does not distinguish between different aboveground exposed crops and is, therefore, not contained in the sum. Further note that the production rate needs to be distributed from administrative units to zones, denoted by n and z respectively (cf. sections B.6 and B.2 on the respective spatial differentiation). This is done on an area-weighted basis.

Remaining atmospheric deposition to agricultural soil

The combined root uptake and harvest process can be regarded as an additional removal process. In the case of atmospheric deposition and harvest, however, one takes out a portion of processes that connects two compartments (air and soil), i.e., wet and dry atmospheric deposition. In order not to violate the mass conservation principle by taking out portions of the atmospheric wet and dry deposition due to harvest of aboveground exposed plant parts, the remaining input from air to soil due to atmospheric deposition needs to be defined. It shall, furthermore, be challenged whether it could possibly assume non-realistic values, i.e., become negative. The amount of atmospheric dry deposition that reaches the soil $S_{\text{a-j,effective dry atmospheric deposition}}$ is given according to Eq. (A-63). The respective amount of atmospheric wet deposition that reaches the soil $S_{\text{a-j,effective wet atmospheric deposition}}$ is defined accordingly (Eq. (A-64)). For the meaning of the symbols, refer to the previous sections.

$$
\begin{aligned}
S_{a\text{-}j,\ \text{effective dry atmospheric deposition}} &= S_{a\text{-}j,\ \text{dry atmospheric deposition}} + \\
&\quad S_{\text{a, dry deposition + harvest exposed crops}} \\
&= ATMDEP_{\text{dry}}(s, p, z) \cdot \\
&\quad \left\{ A(z) \cdot fr\_\text{A}(i, z) - emp_{\text{plant surface loss}}(r, e) \right\} \cdot \\
&\quad \sum_x \left[\frac{fr\_w_{\text{intercept deposition}}(x, e) \cdot P(x, n)}{Y\_fw(x, n, e)} \right] \Bigg\}
\end{aligned}
\tag{A-63}
$$

$$
\begin{aligned}
S_{a\text{-}j,\ \text{effective wet atmospheric deposition}} &= S_{a\text{-}j,\ \text{wet atmospheric deposition}} + \\
&\quad S_{\text{a, wet deposition + harvest exposed crops}} \\
&= ATMDEP_{\text{wet}}(s, p, z) \\
&\quad \left\{ A(z) \cdot fr\_\text{A}(i, z) - emp_{\text{plant surface loss}}(r, e) \cdot \right. \\
&\quad \sum_x \left[\frac{P(x, n)}{Y\_fw(x, n, e)} \cdot fr\_w_{\text{intercept deposition}}(x, e) \cdot \right. \\
&\quad \left. \left. fr\_w_{\text{adhere wet deposition}}(p, x, e) \right] \right\}
\end{aligned}
\tag{A-64}
$$

The mass conservation principle would be violated if the term in braces became smaller than zero. This situation would occur if the area of the compartment was smaller than the product of the empirical plant surface loss factor and the sum in the equations above, i.e.:

$$
A(z) \cdot fr\_\text{A}(i, z) < emp_{\text{plant surface loss}}(r, e) \cdot \sum_x \left[\frac{fr\_w_{\text{intercept deposition}}(x, e) \cdot P(x, n)}{Y\_fw(x, n, e)} \right] \tag{A-65}
$$

$$
\begin{aligned}
A(z) \cdot fr\_\text{A}(i, z) < \quad & emp_{\text{plant surface loss}}(r, e) \cdot \sum_x \left[\frac{P(x, n)}{Y\_fw(x, n, e)} \cdot \right. \\
& \left. fr\_w_{\text{intercept deposition}}(x, e) \cdot fr\_w_{\text{adhere wet deposition}}(p, x, e) \right]
\end{aligned}
\tag{A-66}
$$

It shall be explored when this would be the case by a worst case approach in which the right hand side assumes values as large as possible. The parameters 'mass fraction of a substance that is intercepted' and 'mass fraction of a substance's wet deposition that adheres to aboveground exposed produce' can at most become equal to one and are, hence, disregarded in this discussion. Both inequations become identical in this case. The following equation, therefore, needs to be fulfilled in order to obey the mass conservation principle:

$$A(z) \cdot fr\_A(i,z) > emp_{\text{plant surface loss}}(r,e) \cdot \sum_x \frac{P(x,n)}{Y\_fw(x,n,e)} \tag{A-67}$$

$$\frac{A(z) \cdot fr\_A(i,z)}{\sum_x \frac{P(x,n)}{Y\_fw(x,n,e)}} > emp_{\text{plant surface loss}}(r,e) = \frac{1 - 10^{(r_{\text{plant surface loss}}(r,e) \cdot t_{\text{exposure duration}}(r,e))}}{r_{\text{plant surface loss}}(r,e)} \tag{A-68}$$

If the exposure duration was zero, the numerator of the empirical factor would become zero which would not constitute a problem. The other extreme would be that the numerator assumes a value close to one. In order to guarantee that in any case not more of a substance is removed than is actually deposited on the crops, this upper boundary limit of the numerator is considered:

$$\frac{A(z) \cdot fr\_A(i,z)}{\sum_x \frac{P(x,n)}{Y\_fw(x,n,e)}} > \frac{1}{r_{\text{plant surface loss}}(r,e)}. \tag{A-69}$$

The parameters 'annual production rate', 'cropland area' and 'yield of aboveground exposed produce' are interlinked in that only a certain cropland area ($A \cdot fr\_A$) can sustain an annual production rate (P) given the crop and location-specific yield (Y). A side-condition is that a crop is only once produced on a given area within the balancing period. If this was not the case the yield would need to be increased to obtain a yield integrated over a one year period. The annual production rate and the yield can be rewritten as:

$$P = M_{\text{crop x}} \cdot t_{\text{balance}}$$
$$Y\_fw = \frac{M_{\text{crop x}}}{A_{\text{crop x}}} \qquad \text{(A-70)}$$

Assuming that only aboveground exposed produce was grown on the available agricultural area (i.e., $A(z) \cdot fr\_A(i,z) = A_{\text{crop x}}$) which is again an upper bound estimate, rarely the case at municipal levels or higher for which the production data are given (cf. section B.6.1), the left hand side assumes its smallest value which corresponds to the time over which the production balance is performed, i.e., the duration of one year:

$$t_{\text{balance}} > \frac{1}{r_{\text{plant surface loss}}(r, e)}$$
$$r_{\text{plant surface loss}}(r, e) > \frac{1}{t_{\text{balance}}} = \frac{1}{1 \text{ year}} = \frac{1}{31536000 \text{ seconds}} \qquad \text{(A-71)}$$

Thus, as long as the plant surface loss rate is larger than the inverse of a one year period (here: in seconds), the removal of parts of the atmospheric deposition can be formulated in the way presented without violating the mass conservation principle. United States - Environmental Protection Agency (1998) suggests to use a value of 18 per year which fulfils this condition.

A.7 Exposure assessment

Two exposure assessment frameworks are presently implemented in WATSON. One is from the health physics (radionuclides) context (International Atomic Energy Agency, 2001) and the other concerned with hazardous air contaminants (United States - Environmental Protection Agency, 1998). Equations for both exposure assessment frameworks are given below as far as they are implemented. Some parameter values may depend on the exposure assessment employed which is denoted by an *e* in the brackets after the parameter's symbol in the equations to come.

Different exposure pathways are considered. Here, *exposure pathway* (or *food chain*) means any combination of (a) an environmental medium concentration as predicted by the fate model (e.g., agricultural soil concentration) based on which (b) different interrelated intermediate food concentrations are derived (e.g., wheat consumed by cow, milk) finally being (c) taken in by humans. This brings about that human exposure for example to milk is composed of the expo-

sure pathways based on the ingestion of soil particles, forage, silage and grains by milk cattle. Each of the linkages or steps of an exposure pathway is termed an *exposure transfer*, i.e., a transfer from one medium, substrate, or receptor to another.

The calculation of the different exposure pathways principally may start with a unit conversion of the environmental fate results (section A.7.1). The different steps or exposure transfers of each of the exposure pathways are not shown separately below. Rather, these are aggregated into an overall equation that relates the concentration in the media as assessed by the environmental fate model to those in the different food items for each of the exposure pathways considered (section A.7.4 and following). These concentrations in the different food items are converted by a human consumption rate into the effective personal intake rate (section A.7.14) after taking trade of the respective food or potentially feed items into account (section A.7.13).

Note that when calculating dynamically, the initialization of the environmental fate concentrations needs special treatment which is presented in section A.7.3.

Further note that the intake rates provided in the following sections need to be multiplied by the population at the respective administrative unit in order to yield the overall mass taken up which is used for the computation of the (effective) Intake Fraction (cf. Eq. (7-3)).

A.7.1 Concentration conversion

The environmental fate model results in bulk concentrations that are given in weight of a substance per volume of a medium (kg per m^3). However, many of the equations in the exposure assessment of terrestrial food chains are based on concentrations that are given in weight of a substance per (dry or fresh) weight of the medium (kg per kg FW or kg per kg DW) according to United States - Environmental Protection Agency (1998). The food chains in the aquatic environment, in contrast, are based on the dissolved fraction of the substance. Consequently, different unit conversions need to be performed.

Conversion bulk soil to solid phase concentration

In the terrestrial environment, especially the transfer from soils into aboveground plant parts but also the ingestion of soil particles is based on bulk solid phase concentrations of the dried soil. The conversion from bulk concentrations (kg per m^3) into dry weight concentrations (kg per kg DW) for the compartments arable land (*i*: ag) and pastures (*i*: p) is performed according to:

$$C\_w/dw(i,z) = \frac{1}{fr\_V_{\text{solid phase bulk}}(i) \cdot \rho_{\text{solid phase}}(i,z)} \cdot C\_w/v(i,z) \quad \text{(A-72)}$$

where

C_w/dw : concentration of a substance in compartment *i* of zone *z* [$kg_{chemical}$ per $kg_{solid\ phase}$ DW]

C_w/v : volumetric concentration of a substance in compartment *i* of zone *z* [$kg_{chemical}$ per $m^3_{bulk\ compartment}$] (result from the environmental fate model)

fr_V : volume fraction of compartment *i* that is solid phase [$m^3_{bulk\ compartment}$ per $m^3_{solid\ phase}$] (defined in section 5.1.3)

ρ : density of the solid phase in compartment *i* of zone *z* [kg_{solid} per m^3_{solid}] (defined by Eq. (B-10)).

Conversion bulk soil to solid phase concentration divided by solid-water partitioning coefficient

In the terrestrial environment, the transfer from soils into belowground produce is modelled based on the Root Concentration Factor (RCF). It relates the concentration of a substance in roots to its concentration in soil pore water. In order to use the concept of the RCF for substances that are not metals, the bulk concentration needs to be converted into the dissolved phase concentration according to United States - Environmental Protection Agency (1998) (cf. section A3.4.1). Note that for metals the so-called 'Plant-Soil Bioconcentration Factor in Root Vegetables' is used and consequently requires a different concentration conversion (see above). The conversion from bulk concentrations (kg per m^3) into aqueous phase weight concentrations (kg per kg of aqueous phase) for non-metals present in the compartments arable land (*i*: ag) and pastures (*i*: p) is, thus, performed according to:

$$C\_w/w_{i,\text{aqueous}} = \frac{1}{fr\_V_{\text{solid phase/bulk}}(c) \cdot \rho_{\text{solid phase}}(c,z) \cdot K_{sw,p} \cdot \rho_{\text{water}}(c)} \cdot C\_w/v_i \quad \text{(A-73)}$$

where

C_w/dw : concentration of a substance in compartment *i* of zone *z* [$kg_{chemical}$ per $kg_{solid\ phase}$ DW]

C_w/v : volumetric concentration of a substance in compartment *i* of zone *z* [$kg_{chemical}$ per $m^3_{bulk\ compartment}$] (result from the environmental fate model)

fr_V : volume fraction of compartment *i* that is solid phase [$m^3_{bulk\ compartment}$ per $m^3_{solid\ phase}$] (defined in section 5.1.3)

K_{sw} : solid-water partitioning coefficient of substance *p* that may depend on pH or the organic carbon content of the respective compartment [$kg/kg_{solid\ phase}$ per kg/m^3_{water}] (defined in section C.1.1)

ρ : density of the solid phase in compartment *i* of zone *z* [kg_{solid} per m^3_{solid}] (defined by Eq. (B-10)).

Conversion bulk water to dissolved phase concentrations

Transfer of substances from water into freshwater fish depends exclusively on the dissolved fraction of the substance according to the equations 5-48 and 5-49 given in United States - Environmental Protection Agency (1998). The conversion from bulk concentrations (kg per m^3 of bulk compartment) into concentrations in the dissolved phase (kg per m^3 of aqueous phase of the compartment) for non-metals in freshwater bodies is, thus, performed according to:

$$C\_w/v_{w,aqueous} = \frac{1}{K_{sw,p} \cdot ED_{bulk/solid} \cdot \rho_{suspendend\ matter}(w)} \cdot C\_w/v_{w,bulk} \qquad \text{(A-74)}$$

where

C_w/v : $C\_w/v_{aqueous}$: concentration of a substance in the aqueous phase of compartment *i* in zone *z* [$kg_{chemical}$ per $m^3_{aqueous\ phase\ of\ compartment}$]

C_w/v_{bulk}: concentration of a substance in compartment *i* of zone *z* [$kg_{chemical}$ per $m^3_{bulk\ compartment}$] (result from the environmental fate model)

ED : equilibrium distribution coefficient of a substance *p* of the respective compartment *i* of zone *z* that may depend on a compartment's pH or organic carbon content [-] (defined in section A.2)

K_{sw} : solid-water partitioning coefficient of substance *p* that may depend on pH or the organic carbon content of the respective compartment [$kg/kg_{solid\ phase}$ per kg/m^3_{water}] (defined in section C.1.1)

fr_V : volume fraction of compartment *i* that is solid phase [$m^3_{bulk\ compartment}$ per $m^3_{solid\ phase}$] (defined in section 5.1.3)

ρ : density of suspended matter [kg_{solid} per m^3_{solid}] (defined in section B.5.4).

A.7.2 Assessment of inhalation exposures

Unlike ingestion, inhalation exposures are assessed with the help of the EcoSense model (European Commission, 1999a). In the case of trace elements, the relevant results are the concentrations in air that are given in microgram per cubic metre which need to be converted into kilogram per cubic metre. These concentrations are multiplied by the affected population in order to yield the accumulated inhalation exposure.

In order to apply the cancer and non-cancer slope factors as given in Tables 7-6 and 7-7, respectively, one needs to convert the accumulated inhalation exposure into an amount taken up. For this, the inhalation rate of the affected people is needed which principally depends on age, gender and body weight (United States - Environmental Protection Agency, 1997c, 1998). Values given in the literature range from 4.5 (United States - Environmental Protection Agency, 1997c) to 23 cubic metres per day (value quoted in Table 9.5 in European Commission, 1999a) for babies and male adults, respectively. Average rates of 20 and 20.6 cubic metres of inhaled air per day are used by United States - Environmental Protection Agency (1998) and Spadaro and Rabl (2004), respectively. The value of 20 cubic metres per day is adopted here although noting that average personal inhalation rates from about 14 to 23 cubic metres per day may be obtained for instance when following the approach taken in section 9.3.2 of European Commission (1999a) and using either the values provided therein or those by United States - Environmental Protection Agency (1997c).

The accumulated exposure as provided by the EcoSense tool is translated into the (effective) Intake Fraction due to inhalation at steady-state by taking the effective portion of the trace element into account according to:

$$IF_{\text{inhalation}} = \frac{fr\_w_{\text{effective/total}}(p) \cdot \frac{INH}{1000^3} \cdot \sum_n C\_w/v_{a,n,\text{bulk}} \cdot Population_n}{S} \qquad \text{(A-75)}$$

where:

1000^3	:	conversion factor [µg per kg]
C_w/v	:	concentration of a substance in the air compartment of administrative unit n [$\mu g_{chemical}$ per m^3]
fr_w	:	mass fraction of substance *p* in air leading to an effect [kg per kg] (defined in Table C-2)
IF	:	(effective) Intake Fraction of a substance due to inhalation [$kg_{effective\ exposure}$ per $kg_{released}$]
INH	:	inhalation rate [m^3 per capita and s]; $2.32 \cdot 10^{-4} \sim 20$ m^3 per capita and day according to United States - Environmental Protection Agency (1998)
Population	:	population at administrative unit *n* [capita]
S	:	source strength of a substance [kg per s].

Note that the accumulated exposure yielded by the sum in the above equation is calculated with the help of the EcoSense software tool.

As for ingestion exposures, the Intake Fraction for inhalation in the dynamic case at time *t* (in full years) is given as:

$$IF_{\text{inhalation,t}} = \frac{fr\_w_{\text{effective/total}}(p) \cdot \frac{INH}{1000^3} \cdot \sum_n \sum_t C\_w/v_{a,n,\text{bulk,t}} \cdot Population_n}{\sum_t S_t} \quad \text{(A-76)}$$

A.7.3 Performing dynamic exposure assessment when removal due to harvest is included in the environmental fate model

In previous sections, processes leading to exposure were described that remove a substance at a certain rate from the environmental fate model. At steady-state and when the removal only affects the exogenous input (cf. sections A.6.5 and A.7.4 related to atmospheric interception), the exposure assessment can be based on the predicted environmental concentrations since the continuous release of a substance to the environment is balanced by all removals. When computing dynamically while considering harvest removals, in contrast, one needs to know how much of a substance has been removed in order to know the 'original' concentration without removal for example by plants. This is because 'original' concentration without removal is actually the concentration to which the process rate applied leading to the (reduced) predicted environmental concentration.

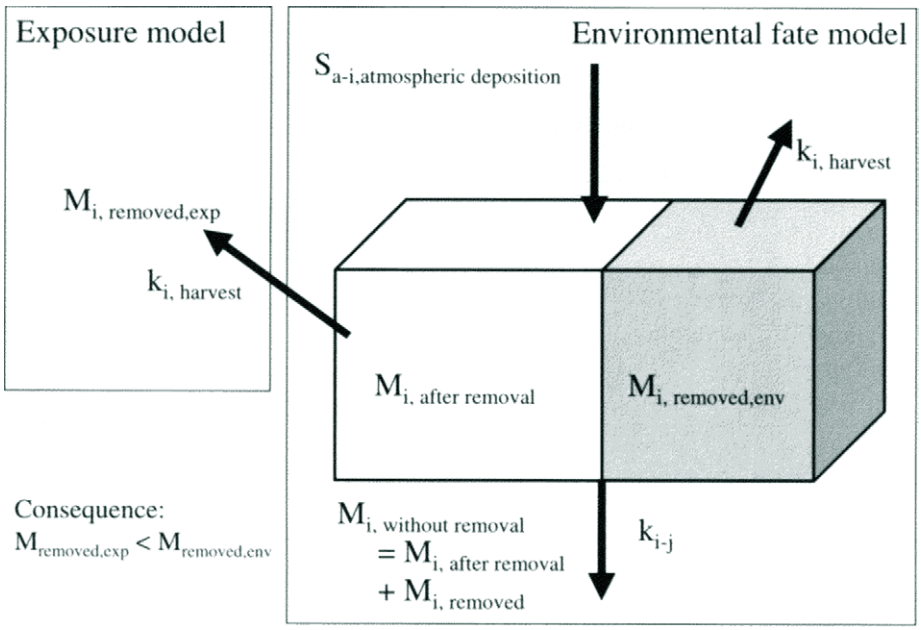

Fig. A-1: Masses with respect to removal due to harvest resulting in the environmental fate and exposure model in the dynamic case

Thus, in order not to assume a transfer rate based on a lower concentration when performing the exposure assessment, one needs to correct the depleted concentrations by the respective removal according to the following equation (cf. Fig. A-1):

$$M_{i,\ without\ removal} = M_{i,\ after\ removal} + M_{removed} \qquad \text{(A-77)}$$

$$C\_w/v_{i,\ without\ removal} \cdot V_i = C\_w/v_{i,\ after\ removal} \cdot V_i + M_{removed}$$

where

C_w/v : $C\_w/v_{i,\ without\ removal}$: concentration that would have occurred in compartment *i* if no removal due to harvest of food had taken place [kg per m^3]

$C\_w/v_{i,\ after\ removal}$: concentration that was predicted by the environmental fate model in compartment *i* [kg per m^3]

M : $M_{removed}$: mass of substance removed [kg]

$M_{i,\ after\ removal}$: mass that was predicted by the environmental fate model in compartment *i* [kg]

$M_{i,\ without\ removal}$: mass that would have been contained in compartment *i* if no removal due to harvest of food had taken place [kg]

V_i : volume of compartment *i* [m^3] (defined in section A.4).

The 'mass of substance removed' can be calculated according to:

$$M_{removed} = C\_w/v_{i,\ without\ removal} \cdot k_{i,\ harvest} \cdot \Delta t \qquad \text{(A-78)}$$

where

C_w/v : concentration that would have occurred in compartment *i* if no removal due to harvest of food had taken place [kg per m^3]

k : process rate of combined uptake by and harvest of the organism [m^3 per s]

$M_{removed}$: mass of substance removed [kg]

Δt : time step of the iteration [s].

The concentration without removal can, thus, be computed as:

$$C\_w/v_{i,\ without\ removal} = C\_w/v_{i,\ after\ removal} + C\_w/v_{i,\ without\ removal} \cdot \frac{k_{i,\ harvest} \cdot \Delta t}{V_i} \qquad \text{(A-79)}$$

$$\Rightarrow C\_w/v_{i,\ without\ removal} = \frac{C\_w/v_{i,\ after\ removal}}{1 - \frac{k_{i,\ harvest} \cdot \Delta t}{V_i}}$$

The computation of the k-values differs for root uptake by belowground and aboveground produce as well as for bioconcentration by freshwater fish (cf. section A.3.8).

Note that the denominator might become zero or negative especially if the volume of the compartment is rather small. WATSON, therefore, checks internally whether the compartment's area share of the respective zone is smaller than the internally set cut-off criterion of 0.5 %. If so, the volume is considered almost negligible and the denominator is set to 0.5 by default.

A.7.4 Food concentration for the exposure pathway 'atmospheric deposition - aboveground exposed produce - humans' for the example of spinach

Although there is little evidence that the amount of substance deposited onto aboveground exposed produce contributes substantially to the overall load contained in a plant (e.g., World Health Organisation, 1992a; Gebel, 1999), this does not mean that exposure due to anthropogenically released substances is not significant via this exposure route. In fact, in EUSES this exposure pathway is not included, at the same time it is noted that "this route may be important for some chemicals" (European Commission, 1996a, p. II-44).

When selecting a crop for an exemplary food chain of this kind, it needs to be borne in mind that

- the produce is grown on open-land and not in a greenhouse (e.g., tomatoes to some extent),
- agricultural practice allows for significant exposure (e.g., cauliflower is protected for a certain amount of time in order not to change its colour to yellow), and
- most of the aboveground plant parts that are eaten are exposed; this is not the case for instance for lettuces and round cabbage.

Spinach appears to comply with all these aspects and has, therefore, been included in the assessment.

The removal from atmospheric deposition builds on the equations presented in section A.6.5 and can be formulated for one type of aboveground exposed produce such as spinach as:

$$C\_w/fw(r, n, p, e) = -[S_{\text{a, dry deposition harvest exposed crops}} + S_{\text{a, wet deposition harvest exposed crops}}] \cdot \frac{1}{P(r, n)} \quad \text{(A-80)}$$

$$= \frac{emp_{\text{plant surface loss}}(r, e) \cdot fr\_w_{\text{intercept/deposition}}(r, e)}{Y\_fw(r, n, e)} \cdot [ATMDEP_{\text{dry}}(s, p, z) + ATMDEP_{\text{wet}}(s, p, z) \cdot fr\_w_{\text{adhere wet deposition}}(p, r, e)]$$

where:

ATMDEP : dry or wet atmospheric deposition of substance p in zone z for scenario s [kg per m^2 per s][41]

emp : empirical correction factor for physical surface loss from plant r [s]

C_w/fw : concentration of substance p in food item r at the administrative unit n [$kg_{chemical}$ per kg_{food} FW]

fr_w : $fr\_w_{adhere/wet\ deposition}$: mass fraction of a substance's p wet deposition that adheres to aboveground exposed produce r [kg per kg]

$fr\_w_{intercept/deposition}$: mass fraction of substance p that is intercepted by aboveground exposed produce r during atmospheric deposition [kg per kg]

P : production rate of crop r in administrative unit n [kg FW per s] (defined as described in section B.6.1)

S : removal of parts of the source of substances (i.e., dry or wet atmospheric deposition) due harvest of exposed aboveground crops [kg per s]; note that the values are negative indicating removal and need, therefore, be subtracted here

Y_fw : yield of aboveground exposed produce r in administrative unit n [kg FW per m^2] (defined as described in section B.6.1).

In contrast to many other exposure pathways, there is no need to convert units of concentrations. However, when calculating dynamically, interception might only occur in specific time periods. In any case, at time zero no emission

[41] See footnote 40 on page 421.

has as yet occurred. Therefore, the atmospheric deposition is set to zero. When assessing a pulse emission, the atmospheric deposition will cease after the pulse emission has terminated plus the length of the residence time of the respective substance in air. As a consequence, the atmospheric deposition after this time period also needs to be set to zero. The trace elements considered here occur in the atmosphere usually attached to particles. Particles of intermediate size show the longest residence times that are typically in the order of days (Jaenicke, 1998). Thus, the residence times in air can be neglected as pulse emissions of a one year period are usually considered (cf. Chapters 10 and 11).

A.7.5 Food concentration for the exposure pathway 'atmospheric deposition - forage/silage - cattle - humans'

Potentially, forage and silage like any other exposed aboveground produce may be exposed due to atmospheric deposition as well. However, the exposure pathways related to silage and/or forage exposure followed by transfer into dairy milk and beef/veal are not included into the assessment. This is due to the fact that (spatially-resolved) information especially on production data are not readily available for silage and forage which is necessary to compute this exposure pathway (cf. section A.7.4).

A.7.6 Food concentration for the exposure pathway 'arable land - aboveground protected produce - humans' for the example of cereals

The exposure pathway 'arable land - aboveground protected produce - humans' is based on the unit-converted concentration in the arable land compartment. At present only the cereals wheat, barley, rye and oats are considered. The related equation when following the exposure assessment provided by United States - Environmental Protection Agency (1998) reads:

$$C\_w/fw(r, n, p, e) = BCF\_dw/dw_{\text{plant/soil}}(p, r, e) \cdot fr\_w_{\text{solid phase/bulk}}(r, e) \cdot C\_w/dw_{\text{ag.solid}} \quad \text{(A-81)}$$

and the one according to International Atomic Energy Agency (2001) is:

$$C\_w/fw(r, n, p, e) = BCF\_dw/fw_{\text{plant/soil}}(p, r, e) \cdot C\_w/dw_{\text{ag.solid}} \quad \text{(A-82)}$$

where

BCF_dw/dw: bioconcentration factor of substance p due to crop r uptake from soil [kg_{soil} DW per kg_{plant} DW] (defined in section C.2)

BCF_dw/fw: bioconcentration factor of substance p due to crop r uptake from soil [kg_{soil} DW per kg_{plant} FW] (defined in section C.2)

C_w/fw : concentration of substance p in food item r at the administrative unit n [$kg_{chemical}$ per kg_{food} FW]

C_w/dw : concentration of substance p in arable land ag of zone z [$kg_{chemical}$ per $kg_{solid\ phase}$ DW] (unit-converted result of the environmental fate model)

fr_w : mass fraction of dry weight per fresh weight of food item r [kg_{food} DW per kg_{food} FW] (defined in Table B-22).

A.7.7 Food concentration for the exposure pathway 'arable land - aboveground exposed produce - humans'

As stated in section A.7.4, the only aboveground exposed produce considered is spinach. The assessment of root uptake follows that for aboveground protected produce given by Eq. (A-81).

A.7.8 Food concentration for the exposure pathway 'arable land - belowground produce - humans' for the example of potato

The exposure pathway 'arable land - belowground produce - humans' is based on the unit-converted concentration in the arable land compartment. Presently only potatoes are considered. The related equation when following the exposure assessment for metals provided by United States - Environmental Protection Agency (1998) reads:

$$C\_w/fw(r, n, p, e) = emp_{\mathrm{BCF,\ root\ crops}}(p, r, e) \cdot BCF\_dw/dw_{\mathrm{root/soil}}(p, r, e) \cdot fr\_w_{\mathrm{solid\ phase/bulk}}(r, e) \cdot C\_w/dw_{\mathrm{ag,\ solid}} \quad \text{(A-83)}$$

and the one according to International Atomic Energy Agency (2001):

$$C\_w/fw(r, n, p, e) = BCF\_dw/fw_{\mathrm{plant/soil}}(p, r, e) \cdot C\_w/dw_{\mathrm{ag,\ solid}} \quad \text{(A-84)}$$

where

BCF_dw/dw: bioconcentration factor of substance *p* due to crop *r* uptake from soil [kg_{soil} DW per kg_{plant} DW] (defined in section C.2)

BCF_dw/fw: bioconcentration factor of substance *p* due to crop *r* uptake from soil [kg_{soil} DW per kg_{plant} FW] (defined in section C.2)

C_w/dw : concentration of substance *p* in arable land *ag* of zone *z* [$kg_{chemical}$ per $kg_{solid\ phase}$ DW] (unit-converted result of the environmental fate model)

C_w/fw : concentration of substance *p* in food item *r* at the administrative unit *n* [$kg_{chemical}$ per kg_{food} FW]

fr_w : mass fraction of dry weight per fresh weight of food item *r* [kg_{food} DW per kg_{food} FW] (defined in Table B-22)

emp : empirical correction factor for equilibrium uptake of substance *p* by belowground produce *r* dependent on the substance's octanol-water partitioning coefficient (K_{ow}) [-] (defined in Table C-6).

A.7.9 Food concentration for the exposure pathways 'pasture/arable land - feed - milk cattle - humans'

The exposure pathways 'pasture/arable land - feed - milk cattle - humans' are based on the unit-converted concentration in the pasture and arable land compartment, respectively. To be more specific, 'feed' could mean forage, silage, or grains. These either grow on pastures (forage) or on arable land (silage and grains).

When following the exposure assessment provided by United States - Environmental Protection Agency (1998), the related equation for silage and forage reads:

$$C\_w/fw(r, n, p, e) = \{ING_{feed}(r_{animal}, e) \cdot BTF\_t/w_{milk/feed}(p, r_{animal}, e)\} \cdot BCF\_dw/dw_{plant/soil}(p, r_{plant}, e) \cdot C\_w/dw_{p|ag,solid} \quad \text{(A-85)}$$

The one for grains for which only wheat is presently considered is formulated as:

$$C\_w/fw(r, n, p, e) = fr\_w_{\text{wheat/total grain}}(r_{\text{animal}}, e) \cdot \{ING_{\text{feed}}(r_{\text{animal}}, e) \cdot BTF\_t/w_{\text{milk/feed}}(p, r_{\text{animal}}, e)\} \cdot BCF\_dw/dw_{\text{plant/soil}}(p, r_{\text{plant}}, e) \cdot C\_w/dw_{\text{ag,solid}} \quad \text{(A-86)}$$

Note that the 'soil bioavailability factor' and the 'metabolism factor' are not considered in Eqs. (A-85) and (A-86) as the recommended values are 1 (ibid., sections 5.4.4.6 and 5.4.4.7).

Only the exposure pathway 'pasture - forage - milk cattle - humans' is presently implemented for the IAEA exposure assessment (International Atomic Energy Agency, 2001):

$$C\_w/fw(r, n, p, e) = \frac{BTF\_t/v_{\text{milk/feed}}(p, r_{\text{animal}}, e) \cdot ING_{\text{forage}}(r_{\text{animal}}, e)}{\rho_{\text{food}}(r, e)} \cdot BCF\_dw/dw_{\text{plant/soil}}(p, r_{\text{plant}}, e) \cdot C\_w/dw_{\text{p, solid}} \quad \text{(A-87)}$$

where

BCF_dw/dw: bioconcentration factor of substance p due to crop r uptake from soil [kg_{soil} DW per kg_{plant} DW] (defined in section C.2)

BTF_t/v : biotransfer factor relating the amount of substance p contained the feed's volume taken in by animal r [s · capita per m^3] (defined in section C.2)

BTF_t/w : biotransfer factor relating the amount of substance p contained the feed's mass taken in by animal r [s · capita per kg FW] (defined in section C.2)

C_w/dw : concentration of substance p in arable land ag of zone z [$kg_{chemical}$ per $kg_{solid\ phase}$ DW] (unit-converted result of the environmental fate model)

C_w/fw : concentration of substance p in food item r at the administrative unit n [$kg_{chemical}$ per kg_{food} FW]

fr_w : mass fraction of grains fed to farm animals r consisting of wheat [-] (defined in Table B-23)

ING : ingestion rate of feed taken in by animal r [kg DW/capita/s] (defined in section B.6.3)

ρ : density of food (milk) [kg per m^3]; here: 1030.

Unlike the other exposure pathways, trade may not only be considered for the animal product that is finally consumed by the human population. Rather, also feed may be traded prior to consumption by the farm animals. This is especially the case for grains. Trade of grains is considered analogously to the trade of food items (cf. section A.7.13).

A.7.10 Food concentration for the exposure pathways 'pasture/arable land - feed - beef and veal cattle - humans'

The exposure pathways 'pasture/arable land - feed - beef cattle - humans' are computed analogously to the equations given in section A.7.9. The only adaptation that needs to be made is to choose the adequate BCF, BTF and feed ingestion values for beef cattle instead of milk cattle.

A.7.11 Food concentration for the different exposure pathways 'pasture (soil particles) - animal products - humans'

The exposure pathways 'pasture (soil particle) - animal products - humans' are based on the unit-converted concentration in the pasture compartment. To be more specific, 'animal products' could mean cattle milk, beef and veal, poultry meat, eggs from laying hens as well as pork.

The related equation when following the exposure assessment provided by United States - Environmental Protection Agency (1998) reads:

$$C\_w/fw(r, n, p, e) = fr\_w_{\text{free-range total}}(r, n, e) \cdot C\_w/dw_{\text{p, solid}} \cdot [BTF\_t/w_{\text{animal product feed}}(p, r, e) \cdot ING_{\text{soil}}(r, e)] \quad \text{(A-88)}$$

where

C_w/dw : concentration of substance p in arable land ag of zone z [$kg_{chemical}$ per $kg_{solid\ phase}$ DW] (unit-converted result of the environmental fate model)

BTF_t/w : biotransfer factor relating the amount of substance p entrained by soil particles (or any other mass like feed) taken in by animal r [s · capita per kg FW] (defined in Table C-5 of section C.2)

fr_w : mass fraction of produce stemming from animals r kept in the free-range at administrative unit n [kg per kg] (defined in section 7.1.1)

ING : ingestion of soil by the animal r [kg DW/capita/s] (defined in section B.6.3).

Note that the 'soil bioavailability factor' and the 'metabolism factor' are not considered in Eq. (A-88) as the recommended values are 1 (ibid., sections 5.4.4.6 and 5.4.4.7).

A.7.12 Food concentration for the exposure pathway 'freshwater - fish - humans'

The exposure pathway 'freshwater - fish - humans' is based on the unit-converted concentration in the arable land compartment.

The related equation when following the exposure assessment provided by United States - Environmental Protection Agency (1998) reads:

$$C\_w/fw(r, n, p, e) = BCF\_V/fw_{\text{fish/water}}(p, r, e) \cdot C\_w/v_{w,\text{aqueous}} \qquad \text{(A-89)}$$

where

C_w/fw : concentration of substance p in food item r at the administrative unit n [$kg_{chemical}$ per kg_{food} FW]

C_w/v : concentration of a substance in the aqueous phase of compartment i in zone z [$kg_{chemical}$ per $m^3_{\text{aqueous phase of compartment}}$] (unit-converted result of the environmental fate model)

BCF_V/fw : bioconcentration factor of substance p due to fish r uptake from water [$m^3_{\text{aqueous phase}}$ per kg_{fish} fresh weight] (defined in section C.2).

For non-lipophilic substances, only uptake from the water body into freshwater fish is relevant according to United States - Environmental Protection Agency (1998) (cf. section 5.7.5.3). The fish concentration of metals other than mercury consequently only results from the transfer from the dissolved phase of the substance in the water body.

A.7.13 Consideration of trade

From trade statistics (Food and Agriculture Organization of the United Nations - Statistics Division, 2002a), it is obvious that the net trade of certain food products differs between countries. This may lead on the one hand to higher exposures even at the society level if the food items produced in a country show a higher

contaminant load while at the same being exported to a small extent. On the other hand, rather active trade relationships between countries will lead to exposures of people that may live at quite some distance from the contaminated environment in case of more localised sources.

In order to consider trade in an exposure pathway, it may be specified for each of the respective exposure transfers whether it involves trade. At present, trade is assumed to lead to homogeneous concentrations in food in general and also in certain types of feed across the geographical scope of WATSON. This 'homogenisation' may occur even more than once for an exposure pathway (e.g., both the wheat and the milk from the exposure pathway 'arable land - wheat - cattle milk - humans' is allowed to be traded). In future developments, a more detailed approach may be realized in which the amounts that are eaten nationally are distinguished from those transported across national borders. An aggregation at least at the national level is suggested as food consumption/supply data are only provided at this level within WATSON (see below and section B.6.2). There may be produces, however, that are not produced in one country but may as well be eaten in the respective country. This is the case for spinach for example. One cannot do without trade between countries in such instances unless one takes the risk to underestimate the overall exposure. The consideration of trade is, therefore, strongly recommended albeit its present initial status of consideration.

The transfer from an environmental compartment into an organism and from organism to organism is based on an equilibrium approach according to United States - Environmental Protection Agency (1998). When trade is assumed to occur, the predicted concentrations in the different food items are first multiplied by the production (or stock) occurring in the respective region. This production may be zero which is why the concentration predicted to this end is termed 'theoretical'. Then, the resulting substance masses given for the different administrative units are added and divided by the production of the reference area. This reference area could possibly be a country, but is at present the entire area covered by WATSON as given in Fig. B-1. Eq. (A-90) shows the involved calculation when trade is considered:

$$C\_w/fw(r, Europe, p, e)_{\text{average}} = \frac{t_{\text{year}} \cdot \sum_n C\_w/fw(r, n, p, e)_{\text{theoretical}} \cdot P(r, n)}{t_{\text{year}} \cdot \sum_n P(r, n)} \qquad \text{(A-90)}$$

where

C_w/fw : C_w/fw_{average}: average concentration of substance *p* in food item *r* in the geographical scope of the assessment ('Eu-

rope') as a result of considering production data [$kg_{chemical}$ per kg_{food} FW]

C_w/$fw_{theoretical}$: concentration of substance *p* in food item *r* at the administrative unit *n* which is theoretical as this concentration may be assessed to occur in an administrative unit in which no respective food item is produced [$kg_{chemical}$ per kg_{food} FW] (defined in sections A.7.4 through A.7.12)

P : production rate of crop *r* in administrative unit *n* [kg FW per s] (defined as described in section B.6.1)

t : time for which the production rate is given [s], i.e., corresponding to one year.

This production-based weighting scheme leads to homogeneous concentrations of the food and feed items across the reference area. The human consumption of the respective food items is calculated according to nationally provided consumption data (cf. section B.6.2).

A.7.14 Computation of the effective personal intake rate from food concentrations

In order to arrive at the effective personal intake rate related to a respective exposure pathway, the corresponding fresh weight concentration in a food item is multiplied by the human consumption rate. As is discussed in more detail in sections 7.2 and B.6.2, furthermore, the amount of the food supply not consumed, the degree of the European food self-supply, and the portion of the substance potentially leading to an effect are taken account of:

$$IR\_p(r, n, p, e) = fr\_w_{\text{effective/total}}(p, r, e) \cdot ING_{\text{human supply}}(r, n) \cdot fr\_w_{\text{self-supply}}(r, e) \cdot (1 - fr\_w_{\text{not consumed/food supply}}(r, e)) \cdot C\_w/fw(r, n, p, e) \quad \text{(A-91)}$$

where

C_w/fw : concentration of substance *p* in food item *r* at the administrative unit *n* [$kg_{chemical}$ per kg_{food} FW] (defined in sections A.7.4 through A.7.12, note the comments in section A.7.13)

fr_w : $fr\_w_{effective/total}$: mass fraction of substance *p* contained in food *r* leading to an effect [kg per kg] (defined in Table C-2)

$fr\_w_{self\text{-}supply}$: mass fraction of produce *r* produced in the geographical scope of the assessment [kg per kg] (defined in section B.6.2)

$fr\_w_{not\ consumed/food\ supply}$: mass fraction of (fresh) food that is produced and traded but not consumed [kg per kg] (defined in section B.6.2)

ING : ingestion of food item *r* by humans according to food supply information for the administrative unit *n* [kg FW/capita/s]

IR_p : effective personal intake rate of substance *p* contained in food item *r* by humans at the administrative unit *n* [kg/capita/s].

Trade is considered by averaging the food concentration across Europe prior to consumption according to the produced amounts of foods in the different countries, states, districts and/or municipalities (cf. section A.7.13).

It shall be noted that when the impact assessment is performed in a risk group-specific way (i.e., the dose-response function is given for only a sensitive portion of the population such as asthmatics, children, elderly people) particularly the respective food consumption behaviours also need to be given accordingly (for the explanation of most of the symbols refer to the equation above):

$$IR\_p_{risk\ group}(r(i), n, p, e) = ING_{human\ supply}(r(i), n) \cdot fr\_r_{risk\ group/population}(r(i), n) \cdot fr\_w_{self\text{-}supply}(r, e) \cdot (1 - fr\_w_{not\ consumed/food\ supply}(r, e)) \cdot fr\_w_{effective\ total}(p, r, e) \cdot C\_w/fw(r, n, p, e) \quad \text{(A-92)}$$

where

fr_r : fraction of the population *r* that belongs to a certain risk group *i* in country *n* [-].

In order to compute the effective Intake Fraction, the sum of the effective personal intake rates of all risk groups need to be performed:

$$IR\_p(r, n, p, e) = \sum_i IR\_p_{risk\ group}(r(i), n, p, e). \quad \text{(A-93)}$$

A.8 Impact assessment

The equations used for the impact assessment are already fully contained in the main text. The reader is referred to Eqs. (7-16) through (7-19) in section 7.3.

A.9 Monetary valuation

The equations used for the monetary valuation have already been fully described in the main text. The reader is referred to Chapter 8.