STUDY REPORT 01 / 08 / 2010
DRC-14-141968-04378A

Sets of equations for modelling exposure associated with soil contamination or emissions from an industrial facility

INERIS

maîtriser le risque
pour un développement durable

Sets of equations for modelling exposure associated with soil contamination or emissions from an industrial facility

<u>MINISTRY OF ECOLOGY, SUSTAINABLE DEVELOPMENT AND THE SEA</u>

INTRODUCTION

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GLOSSARY

ACUTE EXPOSURE: Short-term exposure, lasting from a few seconds to a few days.

BACKGROUND CONCENTRATION: Ambient representative concentration of an element, a compound or a substance in a given medium or a given region. It takes account of natural concentrations (natural pedogeochemical background concentration) and those concentrations that may originate from various man-made sources (such as various pollution by fertilisers or pesticides associated with normal agricultural practices or road traffic). It can also be defined as the normal concentration in a given medium, in the absence of local contamination.

BIOACCUMULATION: The process by which a chemical accumulates in a living organism, through the food chain or an ecosystem. Exchange process between a living organism and its medium, leading to higher concentrations within this organism than in its environment or its food.

BIOAMPLIFICATION: Process of successive accumulation of a chemical from the bottom to the top of the food pyramid.

BIOAVAILABILITY: Ability of a chemical present in the environment to be taken up and absorbed by a living organism and availability to interact with this organism's metabolic processes.

BIOAVAILABILITY COEFFICIENT: Fraction of the external dose of a chemical that penetrates into the organism and is available to interact with this organism's metabolic processes.

BIOCONCENTRATION: The process by which a substance accumulates in a living organism, by direct uptake from the surrounding medium. Example: a chemical present in water can be bioconcentrated by fish through the gills and skin.

BIOCONCENTRATION COEFFICIENT: In this document, this expression means the ratio of the concentration in the animal tissue over the concentration in the animal's exposure medium (water for aquatic organisms, food for other animals).

BIOTRANSFER COEFFICIENT: In this document, this expression means the ratio of the concentration in the animal tissue over the daily intake of the animal.

CONCEPTUAL EXPOSURE DIAGRAM: Representation and/or summary description of the site, its environment and its population including all information collected during the survey and diagnostic phases, providing a clear and simplified presentation of the problem encountered on the site studied. The conceptual exposure diagram makes it easier to understand the mechanisms leading to the risks evaluation, particularly the identification of relationships between pollution sources, different transfer and exposure media and neighbouring populations.

CHRONIC EXPOSURE: Persistent, continuous or discontinuous exposure, produced over a long period, lasting from a year to whole life.

ENVIRONMENTAL MEDIA: Environmental media means the air, ground water, surface water, soil or sediments.

EXPOSURE MEDIA: Exposure media means specifically the media with which the receptor studied is in contact. For human populations, for example, this may be the air inside dwellings, water from the tap, the top soil, or food.

EXPOSURE PATHWAY: Pathway of a substance from the source towards a receptor. An exposure pathway includes a source, an exposure point and an exposure route. If the exposition point is different from the source, there is also a transfer mechanism and an intermediate compartment where the pollutant is transported (eg. ingestion of self-grown vegetables).

EXPOSURE ROUTE: Route by which a chemical penetrates into the organism. There are three different exposure routes: inhalation, ingestion and dermal contact, which can be differentiated depending on the transfer medium involved:

- inhalation of a chemical as a gas or absorbed onto dust, or diluted in water vapour,

- direct ingestion of soil, foods (plants grown on the site, animals reared on the site), or contaminated water,

- dermal absorption by contact with a contaminated soil, dust and/or water (bath, shower, sailing, etc.).

EXTERNAL DOSE: Quantity of chemical in contact with the organism's barriers (intestinal walls, lung alveolae, skin). It is generally expressed as weight of substance per unit body weight and per unit time.

GEOCHEMICAL BACKGROUND CONCENTRATION: Natural concentration of an element, a compound or a substance in a given medium, in the absence of all specific external sources, such as those due to human activity.

INTAKE: Quantity of chemical provided to an organism and in contact with this organism's barriers (intestinal walls, lung alveolae, skin). It is generally expressed as weight of chemical per unit body weight of the organism and time.

NATURAL ATTENUATION: Term covering all processes involved in dispersion, dilution, adsorption and chemical or biological degradation phenomena having the effect of reducing the weight, volume, concentration, availability or toxicity of a source of pollution.

QUANTITATIVE STRUCTURE ACTIVITY RELATIONSHIP (QSAR): Statistical relationship established for a set of chemicals or compounds and used to estimate the value of a parameter for these chemicals or these compounds from their structure or from one or more of their physico-chemical characteristics (eg. relationship giving the bioconcentration coefficient of a chemical in the fish based on this chemical's octanol-water partition coefficient).

RELATIVE BIOAVAILABILITY COEFFICIENT: Ratio of the bioavailability coefficient for a chemical present on a particular matrix over the bioavailability coefficient for this same chemical in a reference form. Example: the relative bioavailability coefficient of lead for soil is generally calculated as the ratio of the bioavailability coefficient of lead ingested from a soil matrix over the bioavailability coefficient of lead ingested as lead acetate.

RESIDUAL RISKS: Risks resulting from exposure to residual concentrations (cf. residual risks analysis).

RESIDUAL RISKS ANALYSIS (ARR): Quantitative evaluation of health risks carried out on residual exposures, i.e. on exposures expected after applying the management plan.

Extract of the circular dated 8 February 2007 on registered facilities (Prevention of soil pollution - Management of polluted soils): "When the characteristics of a management plan enables to not eliminate all possibilities of contact between pollution and people, potential health risks associated with residual exposures must be evaluated and assessed. The residual risks analysis (ARR) is the specific tool for this purpose."

SUB-CHRONIC EXPOSURE: Exposure of intermediate duration between acute exposure and chronic exposure, lasting from a few days to a year.

TRANSFER: Migration of subtances in any form whatever (dissolved, liquid, gaseous) in one or more media (eg. through or at the surface of a soil, caused by water, air and human activities, or even by soil organisms).

UPTAKE: Quantity of chemical penetrating the organism's barriers following contact. It can be estimated as the product of the external dose multiplied by the absorption rate for the chemical. It is generally expressed as weight of chemical per unit body weight of the organism and per unit time.

ABBREVIATIONS

2,3,7,8 TCDD: 2,3,7,8 TetraChloroDibenzoDioxin
BaP: Benzo(a)Pyren
ERS: Health Risks Assessment
PAH: Polycyclic Aromatic Hydrocarbons
ICPE: Facility Registered for Protection of the Environment
PCB: PolyChloroBiphenyls
PCDD: PolyChloroDibenzoDioxins
PCDF: PolyChloroDibenzoFurans
QSAR: Quantitative Structure Activity Relationship
TRV : Toxicological Reference Value

SUMMARY

Human health risks assessment associated with developing a contaminated site or setting up an industrial facility requires the exposure level of the population from different sources and environmental media be modelled, using several transfer and exposure routes for pollutants.

This document presents calculation approaches used by INERIS to assess exposures associated with a polluted site or an industrial facility.

It is split into two parts:

- the first (part A) describes the document's scope of application, offers a general description of the approaches to modelling presented and states the principles an assessor should use as the basis for selecting the right approach;

- for each transfer type and exposure pathway, the second (part B) gives the conceptual model, equations and conditions for using these equations (assumptions, limitations, uncertainties).

  The routes covered in this manual relate to inhalation, ingestion and dermal contact. The environmental and exposure media considered are soils, groundwater, surface water, outdoor air, indoor air, plants, animal products and breast milk.

This document aims to provide practical and relatively simple calculation approaches to answer conventional questions of risk assessment. These approaches must be selected and used depending on the defined conceptual diagram and more generally the context of each study.

On the other hand this document does not describe an integrated model with paired calculation modules, used to represent the mass balance of a pollutant in the environment.

Nor does INERIS claim to provide state-of-the-art modelling. During INERIS'work, modelling approaches may change and this manual may be updated. It will be accompanied by further additional documents to define the parameters used in the equations.

With this manual giving detailed descriptions of the origin of the equations used, the assumptions on which they are based and associated limitations, INERIS wishes to contribute to the development of greater expertise by:

- promoting harmonised practices,

- facilitating the work of risk assessors,

- improving the transparency of studies.

PART A: OBJECTIVE OF THE DOCUMENT AND GENERAL PRESENTATION OF THE MODELS

1. <u>INTRODUCTION</u>

Assessment of health risks associated with developing a contaminated site or setting up an industrial facility requires the exposure level of the population from different sources and environmental media be modelled, using several transfer and exposure routes for pollutants.

There are numerous multimedia exposure models, particularly in the field of contaminated soils, to assess these exposure levels and associated health risks. INERIS has analysed a number of these calculation tools (INERIS: 2001; 2002a, b, c; 2004a; 2007a). However, none of these models appeared complete or suitable enough to meet the needs and special features related to each risk analysis. INERIS has therefore developed its own tools from equations and data available in the literature to complete.

Through risk assessment work carried out at INERIS over fifteen years, certain aspects of modelling transfers and exposures have been analysed or researched more thoroughly than others. Over the years, occasionally different calculation methods have been developed depending on the field of reguulation (Detailed Risks Assessment for contaminated soils, assessment of health risks for Facilities Registered for the Environment, or even risk assessment associated with new or existing substances).

This document aims to summarise the results of this work and to present the calculation approaches selected for the integrated assessment process of exposures associated with a polluted site or an industrial facility, in order to:

- promote harmonised practices,
- facilitate the work of risk assessors,
- contribute to greater transparency of studies.

It does not claim to be state-of-the-art for modelling, but represents current practices at INERIS in this field. Thus, as teams conduct the work and gain experience, these modelling approaches may develop in the future and this document may be updated.

This document is divided into two parts:

- the first (part A) presents the objectives and scope of application of the document, as well as a general description of calculation models developed in the second part;
- for each transfer type and exposure pathway, this second (part B) gives the conceptual model, equations and conditions for using these equations (assumptions, limitations, uncertainties).

This document will be accompanied by further guides and notes to define the parameters used in the equations. Certain parameters can play a very marked role in the models used (Bonnard, 1997; INERIS reports, 2005a; 2006). Guides will present important issues to be considered when defining values and will be able to offer a method for choosing and assigning values to parameters based on the model's sensitivity to these parameters, objectives of the study and the quality of the available data.

2. SCOPE OF APPLICATION OF THE DOCUMENT

The approaches to modelling collected in this document aim to estimate exposure levels and risk levels for a population, associated with an industrial pollution source or contaminated soil, at a local scale.

In regulatory terms, the circular dated 8 February 2007 on registered facilities (Preventing soil contamination - Managing contaminated soil) and the 15 May 2007 circular (BPSPR/2007 – 128/VD) present the assessment of health risks as 'one tool among others for managing chronic risks'. They indicate that the purpose of assessing health risks is to validate the management plan for a contaminated site by analysing residual risks. As part of impact studies for facilities registered for the Environment (ICPE), risk assessment is presented as a tool that should rank action priorities, validate procedural choices and guide the monitoring plan.

The modelling approaches presented in this document can be used to meet these objectives.

Some of these calculation approaches can also be used for specific work, such as comparing results from measurement with those from modelling or identifying a contamination source. However, for such applications, the choice of assumptions must be guided by attention to realism and the calculations should normally be more accurate than those used to check that the residual risks after renovating a site are acceptable. Less conservative, more complete (eg. taking account of pollutant losses incurred by a medium) and more complex approaches can therefore prove necessary.

The equations developed in part B are presented without reference to an exposure duration, to retain their generic nature and enable them to be applied to estimate exposure levels associated with acute exposure[1] (from a few seconds to a few days), sub-chronic exposure[1] (from a few days to a few years) or chronic exposure[1] (from a year to whole life).

On the other hand, this document does not deal with methods for estimating the exposure of workers responsible for decontaminating a site or people working in an operating facility and in direct contact with pollutants. The dispersion of accidental discharges (such as leaks on the surface of or into a soil) are also not covered.

3. DEVELOPMENT OF THE DOCUMENT

This document has been developed in five phases:

- a phase interviewing engineers belonging to different teams in the Chronic Risks Department, working or having worked on modelling exposure from a source of environmental contamination. Teams working on modelling pesticide concentrations in the environment have also been consulted. On the other hand, work associated with exposure of consumers has not been considered.

   This stage lists the relevant calculation tools;

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[1] Definition given by US EPA 1989

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- a writing phase, in which all the corresponding calculation equations have been described. At this time, certain points could be considered in greater depth, in order to specify usage limitations for these models or to formulate them more generally, and so make them applicable to other settings (eg. applying an equation developed for organic substances to inorganic substances);

- an internal review stage;

- a review phase involving external organisations;

- a phase correcting the document and responding to comments made by external reviewers . This work resulted in a second report being drafted, entitled '*Comments from reviewers of the report 'Sets of equations for modelling exposure associated with soil contamination or emissions from an industrial facility', version dated 16/04/09 and responses provided by INERIS',* referenced DRC-10-109450-02656;

At the end of this process, the two documents underwent a final check, which is the specific quality procedure used at INERIS before distributing all reports.

4. OVERVIEW OF ALL ESTIMATION APPROACHES PRESENTED

The method for estimating levels of exposure and risk is shown in the diagram below:
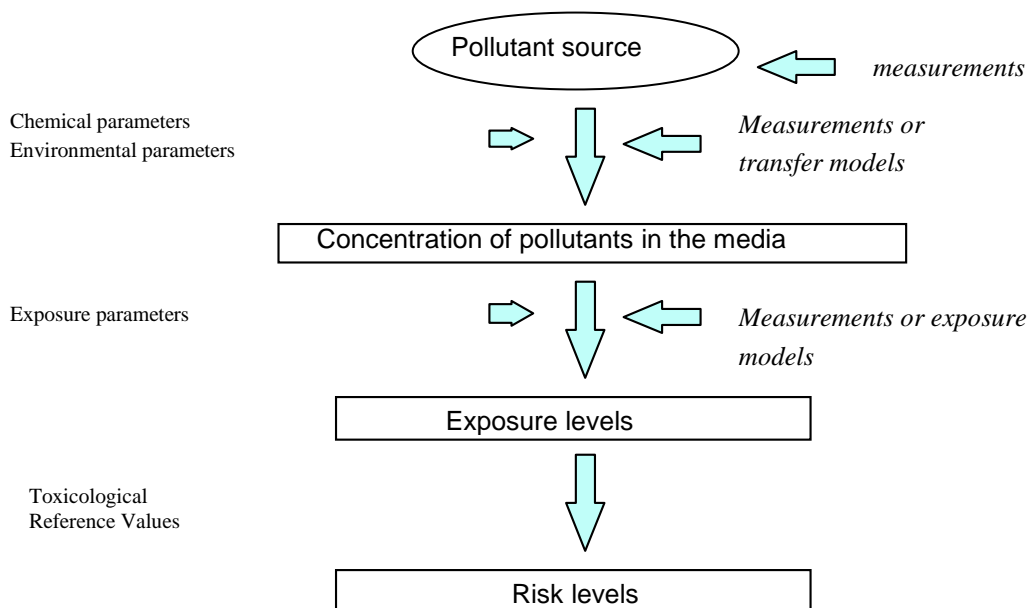
Figure 1: Schematic diagram showing the approach to quantifying exposure

Depending on the available input data, the entire modelling process should be conducted from characterisation of the source, or only one part, from measurements of pollutants in environmental media or measurements in exposure environments[2].

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[2] Under regulations for administering registered facilities (circular dated 8 February 2007 regarding registered facilities - Preventing soil contamination - Managing contaminated soil, circular

Based on the diagram in Figure 1, part B presents sets of equations dedicated to estimating concentrations in media, exposure levels, and risk levels, successively.

But the calculation modules presented do not cover all situations. These modules are sets of equations used by INERIS for health risk assessments, mainly for industrial sites, up to the time this report was written.

Some media (marine environment) or some transfer mechanisms (dispersion of pollutants in an estuary, pollutants returning to the soil in animal faeces or after the death of plants, pollutants in the soil picked up by fluctuation of groundwater level) have not been handled by modelling or only under limited conditions (eg. modelling for pollutant concentrations lower than the solubility limit). As a result, the calculation modules developed are essentially focused on a terrestrial environment, even if one section is devoted to simplified approaches that can be used to handle the outcome of pollutants in groundwater and surface water. Atmospheric dispersion of pollutants is tackled, but the set of equations is not covered explicitly, because while the results are used by INERIS, this part of the study is generally handled separately.

The document deals with the behaviour of contamination, for which the source term can be located in the soil or groundwater, which can consist of an atmospheric point discharge or widely spread in the atmosphere or be a point discharge in surface water. However, methods for estimating these source terms are not covered by this document. In practice, in studies of contaminated soils, the volume and concentration of pollutant from the source are defined from the in-depth diagnostic survey. For ICPE, the ERS is carried out from measurements on the emission flow, estimates based on emission coefficients or from limit values set by local authority bylaws.

Finally, Figure 2 summarises all media, transfer mechanisms and exposure pathways described in part B of the document, schematically.

Figure 3 represents the same thing as a matrix. Each diagonal element of the matrix, items at (i, i), corresponds to one of the media studied and presents the internal processes for this medium i. Items outside the diagonal, items at (i, j) where i ≠ j, describe transfers from medium i to medium j.

The reader will note that, in Figure 3, certain transfer phenomena appear in normal type face while others are in bold face. The mechanisms labelled with normal type face are only covered in part B of the document as pollutant inflow phenomena from upstream medium i to downstream medium j. Those appearing in bold face are covered both as an inflow mechanism from upstream medium i to downstream medium j, and as a loss process for medium i. The phenomena in rectangles representing environmental media (cf. Figure 2) or in (i,i) items of the matrix (cf. Figure 3) are covered in the document only as loss mechanisms for medium i. This applies, for example, to the sedimentation mechanism that appears in the rectangle or box for 'surface water'. This transfer phenomenon has been entered under 'surface water' and not between the 'surface water' and 'sediments' boxes, because the assessor may or may not consider it in the model as a mechanism for

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BPSPR/2007 – 128/VD dated 15 May 2007), the impact of facilities that have operated for several years or of a contaminated site must be based on actual measurements of contamination in different media. These measurements will be interpreted using the medium interpretation approach. In this context, risk will only be calculated firstly if the measurements indicate that exposure media have deteriorated from their initial state, and secondly if there is no regulatory management value for interpreting these measurements.

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losing the pollutant from surface water, but this process is not currently used in the document to estimate the concentration in the sediment layer.

The absence of a link between consideration, on the one hand, of the pollutant inflow from a medium i to a medium j by a transfer mechanism, and consideration of the pollutant loss caused for medium i by this mechanism, on the other hand, is associated with using simplified approaches to modelling (cf. section 5). It does not reconcile the mass balance of pollutant in the environment. But, calculation methods where the losses incurred by a medium (or reduced inflows) are not necessarily considered can be used to obtain cautious estimates of levels of exposure and risks. Uncertainties associated with the fact of having neglected these loss phenomena can then be tested by reintroducing these loss mechanisms or by comparing quantities of pollutant transferred from medium i to medium j with the estimated quantity of pollutant in medium i.

Finally, even if all transfer mechanisms and exposure pathways considered have been grouped in the same matrix, the equations presented for each of these mechanisms may correspond to different, even opposing, calculation conditions or assumptions (eg. approach based on the assumption of one pollutant source in the soil in stationary state for calculating emissions into the air versus an approach considering loss phenomena in the soil to estimate the change in pollutant concentration in the soil over time). These different equations should therefore be selected and used is a structured way, based on the objective of the study and the conceptual model (cf. section 6 in part A).

As a result, figures 2 and 3 offer a summary view of the different transfer mechanisms and exposure pathways covered in part B by means of the different calculation methods developed. But they should not be considered as the schematic representation of an overall model where transfer mechanisms would necessarily be coupled.
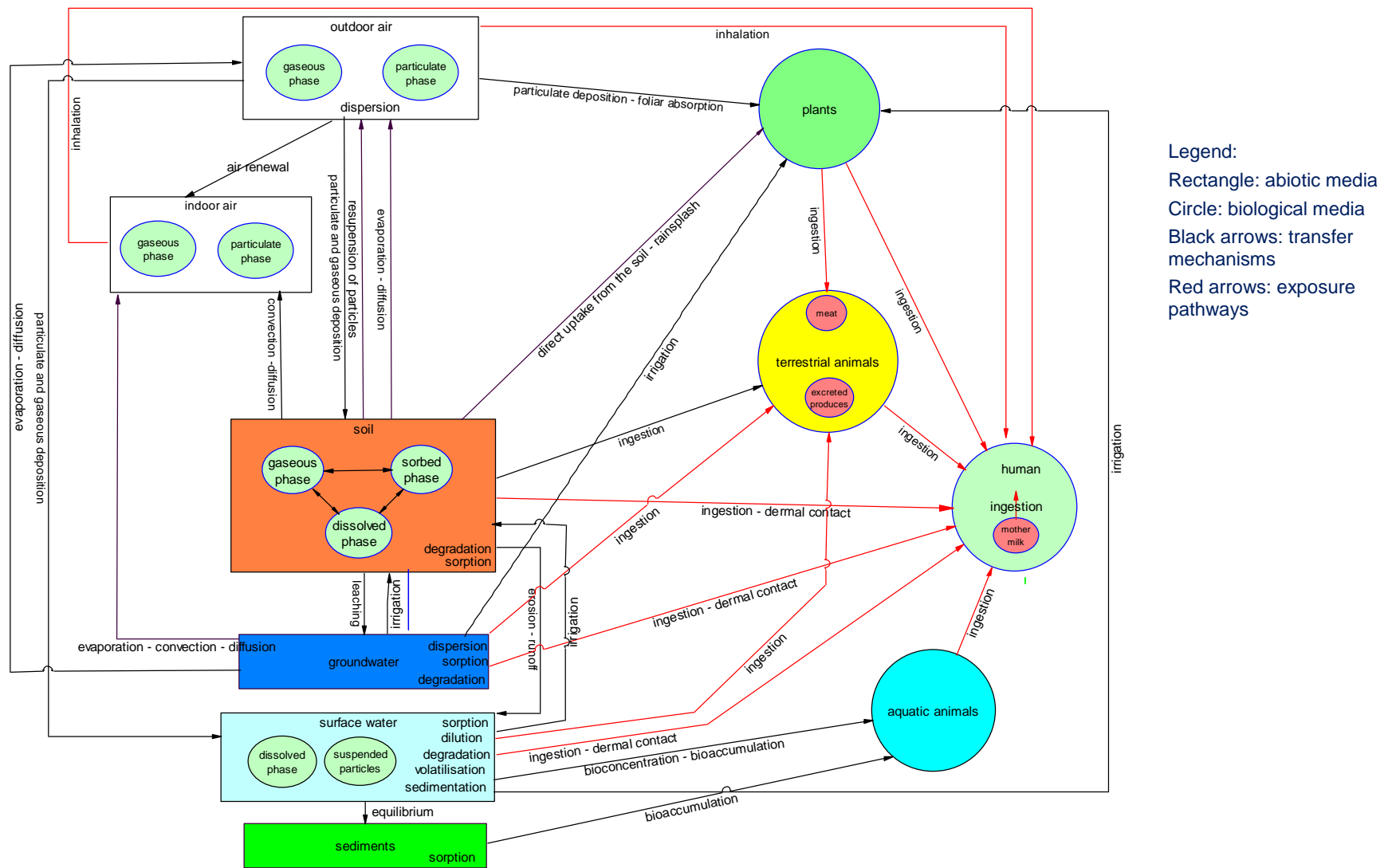
Figure 2: Media, transfer mechanisms and exposure pathways described in the document

Soil Degradation Sorption	**Diffusion** Evaporation Resuspension of particles	Convection Diffusion	**Leaching**	**Runoff** **Erosion**		Direct uptake from the soil Rainsplash	Ingestion	Ingestion Dermal absorption
Particulate and gaseous deposition	**Outdoor air** Dispersion	Air renewal		Particulate and gaseous deposition		Particulate deposition Foliar absorption of gaseous pollutant		Inhalation of gases and particles
		Indoor air						Inhalation of gases and particles
Irrigation	Evaporation Diffusion	Evaporation Convection Diffusion	**Groundwater** Dispersion Degradation Sorption			Irrigation	Ingestion	Ingestion Dermal absorption
Irrigation				**Surface water** Dilution Volatilisation Sedimentation Degradation Sorption	Equilibrium	Irrigation	Ingestion Bioconcentration Bioaccumulation	Ingestion Dermal absorption
					Sediments Sorption		Bioaccumulation	
						Plants	Ingestion	Ingestion
							Animals	Ingestion
								Humans Ingestion of breast milk

Figure 3: Interaction matrix between different media (only mechanisms and pathways considered in part B are shown)

5. CHARACTERISTICS OF CALCULATION MODULES AND EQUATIONS

A good number of the equations used by INERIS are similar or identical to those used in multimedia models, such as HHRAP (US EPA, 2005), RISC (Spence Environmental Engineering, 2004), RBCA Tool Kit (Groundwater Services Inc, 1998) or HESP (van den Berg, 1994). Although the concepts on which these models are based are generally the same, simplifications and assumptions made afterwards often lead to different equations and values of parameters.

In these fairly simple approaches, concentrations in media are estimated by the mathematical representation of convection, diffusion and degradation phenomena. Concentrations in media are generally calculated by considering the concentrations in the upstream medium (media) or sources A, but without taking account of secondary transfers from medium B to medium A. As an example, the transfer from soil to plants (root uptake) is considered, but not the transfer of pollutant from the plant to the soil as leaves fall on the ground. In the same way, the quantity of particulate pollutant arriving at the ground from the air is generally calculated from atmospheric deposition, without deducting the quantity of particles intercepted by plants. Deducting the quantity of particles intercepted by the leaves would have to be compensated by adding the quantity of particles subsequently removed from the leaves, by the action of wind and rain, and by taking account of the plant fraction that ultimately returns to the soil (so as not to underestimate the pollutant concentration in the soil). Considering these phenomena is a delicate balance: their importance depends on numerous factors (pollutant type, size of particles, plant type, weather conditions, plant growth stage) and the data needed to quantify them appears inadequate. The approaches presented in section B are therefore simplified, which may contradict the principal of conservation of mass.

All these equations do not enable an entirely coupled model to be constructed, one that takes account of all transfer mechanisms for a pollutant between different media. For example, in the presence of both an atmospheric VOC emission from the chimney of a facility and a source of VOC in the soil, it is possible using equations from part B to estimate the pollutant concentration inhaled indoors and outdoors, taking account of the dispersion of flux emitted at the chimney and flux emitted from the soil source by convection and diffusion. On the other hand, when the facility is operating, the revolatilisation flux associated with deposited gaseous pollutant cannot be taken into account. However, this flux can be considered as negligible compared to the two others.

The approaches developed in this document are therefore relatively simple, which does not necessarily make it possible to establish a mass balance for a pollutant in the biosphere, but which has the objective of answering questions supporting risk assessments carried out on sites.

In the same way, this document adopts practical methods to estimate exposure that do not represent real transfer phenomena. Thus, to calculate exposure involving a soil layer thickness z (direct ingestion of soil, ingestion of plants), the pollutant concentration in this soil layer is estimated by assuming that the quantity of pollutant deposited on the surface is distributed over this depth.

Even if the quantity of pollutant lost by this layer (eg. by leaching) can be deducted, the pollutant concentration gradient in the layer is not calculated (cf. section 1.1.2 of part B).

On the other hand, contrary to some of the models cited above, this document does not give pollutant concentrations in media only in the steady state. They are often also expressed as a function of time. These expressions can be helpful, particularly for evaluating acute exposures, following the change of concentration in a matrix, taking account of exposure conditions that vary over time, etc. Thus the reader will note that most of the parameters for the equations presented below can themselves be defined as time-dependent parameters (within use limitations specified for these equations and on condition that they are not based on the assumption of reaching the steady state). However, for reasons of readability, the time-dependence of different input parameters is not carried over into the equations presented.

When they exist, analytical solutions for differential equations presented are given, but they can of course be solved numerically.

6. CONDITIONS FOR USING CALCULATION MODULES AND EQUATIONS PRESENTED

As indicated in existing risk assessment guides (MATE, 2000, INERIS, 2003), all the transfer mechanisms and exposure pathways listed have certainly not been modelled in one study. Depending on the use of the site, the characteristics of the pollutant and the site, a site-specific conceptual exposure diagram must be defined. For designing this diagram, the reader should refer to the document from the Ministry for the Environment (MEDAD, 2007c).

From this conceptual model, the study objectives and available resources, appropriate algorithms and equations must be selected for a given study, to build a tool for estimating exposures specific to the study. As stated in the document presenting the Residual Risks Analysis approach (MEDAD, 2007d), "the selection of transfer 'models' and values for associated input parameters (environmental parameters, physico-chemical parameters of substances, soils, etc.) is adapted to the special features of the study".

In the first place, it is necessary to ensure all the phenomena that can contribute to increasing concentrations in exposure media are taken into account. In this way, depending on the type of contamination, some transfer mechanisms will be relevant and others not. For example, for a soil contaminated by volatile pollutants, the transfer of pollutants from the source to the habitat should be considered. There will be a distinction between the pollutant concentration (and therefore exposure by inhalation) outside and inside buildings. For emissions of volatile pollutants from the stacks of an industrial facility, only atmospheric dispersion is modelled, and the concentration inside buildings attributable to the facility can, as a first approximation, be taken as equivalent to the concentration outside. Depending on the properties of chemicals, use of the site, etc., certain exposure pathways are negligible and a quick over-estimated calculation may be enough to demonstrate it. For example, dermal absorption or gas and particle inhalation by animals are exposure pathways that often prove negligible compared to other exposure pathways considered.

Depending on the type of substance, some models may or may not be suitable. Empirical relationships such as QSAR (Quantitative Structure Activity Relationship) are thus established from a group of substances with given physico-chemical characteristics. As an example, substances with a high octanol-water partition coefficient, such as benzo(a)pyrene (BaP) or 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD), do not fall into the valid scope of the modified Potts and Guys relationship, recommended by the US EPA (2004d) to estimate the dermal permeability coefficient for a pollutant through the stratum corneum from water.

In some cases, a deliberately over-estimated approach may be desirable. If the objective is to demonstrate that the residual risk associated with the selected management solution is acceptable, this type of calculation approach, which tends to increase the risk, can be adequate and avoids under-estimating concentrations in the soil or predicted levels in other environmental or exposure media. The representation of certain phenomena can therefore be deliberately omitted, as the assessor favours the principle of caution over the concept of realism. For example, natural attenuation phenomena of pollutants in the soil (such as erosion, runoff, degradation, volatilisation and leaching) can be considered as phenomena contributing pollutants to downstream media (surface water, air, groundwater), but losses incurred by the soil may not then deducted from the soil source.

The complexity of the model to be used must also be assessed in terms of the degree of accuracy required in the results and the resources available to conduct the study.

In this way, taking account of physical, chemical and biological phenomena in the detail can, in some cases, make the model hard to follow. The quest for accuracy and/or realism can work against the objective of transparency in studies.

In addition, the quality of a calculation result depends on both the equations and the input data used being representative. A complex model requires a greater amount of input data. Such a tool, used with sensitive data defined by default, due to a lack of time or money, losses its benefit.

Apart from situations to be defined by the Ministries for the Environment and Health where generic approaches could be employed, using a calculation model needs a case-by-case analysis and therefore the expertise of the assessor.

Thus, several modelling approaches may sometimes be described for the same transfer mechanism in this document. The assumptions and limitations to each approach are presented to make it easier to choose the approach most suited to the study. Presentation of several approaches may also help to assess uncertainties. When scientific knowledge is too limited to favour one model over another, performing a comparative analysis of the results from the different models available is an important factor in assessing uncertainties and therefore the risk characterisation step. Introducing loss phenomena experienced by a medium, during this step, can also be used to test the impact of conservative assumptions made at the start, consisting of ignoring natural elimination or attenuation phenomena for the pollutant.

To meet the needs of a risk assessment for a contaminated site or for emissions from an ICPE, it is therefore possible to use:

- the calculation approaches developed in part B of the document,

- measured values. Measured values generally include background concentrations (of man-made and/or geochemical origin), in addition to the impact of the contamination source studied. These data should therefore be used appropriately for the desired objective (cf. section 4 of part B);

- modelled values derived from more complex mathematical models, if there is a need to do so. The equations described here remain relatively simple. Each medium is represented by one (or more) compartment(s) in which the concentration is assumed to be uniform. The use 1, 2 or 3-dimensional models can prove necessary in certain cases, for example to estimate the transfer of pollutants from the soil to the groundwater or concentrations in the water in a river.

But, in all cases, selecting methods for estimating and interpreting the results obtains should take account of the assumptions on which these approaches are based.

7. <u>METHOD OF PRESENTING EQUATIONS</u>

For each transfer mechanism and exposure pathway, part B of the document describes the physico-chemical and biological phenomena involved, the assumptions and/or simplifications made and the mathematical reasoning leading to the expression of concentration, dose or risk level. To make the final expressions easier to understand and use, without having to refer to another section of the document, each expression is accompanied by a table summarising the parameters used in this expression.

This table is presented in the following form:

Symbol	Parameters	Dimensions	Units	Status
C_{wd}	Concentration dissolved in water	$M.L^{-3}$	$mg.m^{-3}$	C or E

To avoid restricting the validity of the expressions presented to a single system of units, the dimensions are given for each parameter in the equation.

Five fundamental quantities are sufficient to express the dimensions of the different variables making up the equations presented:

- length represented by the symbol L,

- mass represented by the symbol M,

- time represented by the symbol T,

- temperature represented by the symbol K,

- number of moles represented by the symbol Mol.

A set of units traditionally used to define the parameters of the equation is provided as an example. Depending on the study, the total exposure period and the time scale used to define the parameters (daily, monthly, annual, etc.), other units can be employed.

Finally, the status tells the reader if a parameter of an equation:

- should be calculated first: C,
- should be defined as input data: E (it can be a result of measurement or a calculation method outside the estimation approaches described here),
- is defined as data internal to the model: I.

PART B: PRESENTATION OF EQUATIONS

This part of the document presents, successively, the calculation approaches for estimating:

- concentrations in media (section 1),
- exposure levels (section 2),
- risk levels (section 3).

Estimating the pollutant concentration in breast milk (biological medium related to human beings) is covered in the section on exposure levels.

1. ESTIMATING CONCENTRATIONS IN MEDIA

1.1. 'SOIL' MEDIUM

After stopping an industrial activity, the soil medium is often the principal source of exposure. For a facility still in operation releasing atmospheric emissions, exposure (apart from direct pollutant inhalation) depends largely on concentrations in the soil medium, which is an important receptacle for atmospheric contamination. Determining the pollutant concentration in soils is therefore one of the first steps in the process of estimating exposure.

Pollutant flows to other environmental media (air, groundwater, surface water) are estimated from the concentration in soil, as well as contamination of plants and exposure of animals and people by inhalation, ingestion of soil or dermal contact (cf. Figure 2 and Figure 3).

But, depending on the process considered, the soil layer involved is different. To take account of erosion or runoff phenomena, for soil ingestion or dermal contact, we are interested in the surface layer of the soil. For root uptake to plants, the area covered by the plants' roots should be considered. Finally, for gaseous transfer from the soil to the atmosphere or to the air inside a building, pollutants can be mobilised over a much greater thickness. Soil can rarely be considered as homogeneous over its entire depth. Several layers with properties assumed to be uniform (eg. organic carbon content, water content, porosity, etc.) are therefore often defined to represent the soil compartment.

Thus, for the emission of gaseous pollutant from a source located at depth z in the soil into the atmosphere or a building, we consider the pollutant concentration in the soil at the source and the properties of the soil layers located between the source and the emitting surface. In this situation, representing past contamination[3], the concentration in the soil is determined by

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[3] For a future facility or an operating facility, pollutant emissions into the air from a source located deep in the ground, following the accumulation of pollutants deposited on the surface that then migrated in the soil, are not taken into account. They can actually be considered as negligible compared to direct emissions into the air (this assumption might not be verified, only it past emissions that generated pollution deep in the soil were much greater than present or future emissions, but in this case the soil source created should be studied as such).

measurement. For pollutant emission in particulate form into the atmosphere, soil ingestion, dermal contact and root uptake, we are interested in the average pollutant concentration in the soil layer extending from the surface to the depth in question (the depth of soil dug over or worked for transfer to cultivated plants, or the first few centimetres for the other processes cited). As this soil layer may be contaminated from future discharges from an industrial facility, estimating its concentration requires recourse to modelling. This section therefore focuses mainly on estimating the pollutant concentration in a soil layer with its top at the soil surface.

1.1.1. PARTITION OF THE POLLUTANT BETWEEN DIFFERENT PHASES OF THE SOIL

As the soil is a multi-phase medium (air, water, solid) and the future of the pollutant in the soil depends on the distribution of pollutant between these different phases, this section focuses on relationships that can be described between pollutant concentrations in different soil phases.

Depending on the pollutant concentration in the soil, this can be presented in three or four phases. The pollutant in the soil is:

- adsorbed to soil particles,
- dissolved in in the soil porewater,
- as gas in the soil air,
- as an immiscible phase, when the limit of solubility in soil water is reached.

Traditionally, **models are based on the assumption that pollutants are in equilibrium between these different phases and this equilibrium is reached immediately**. This assumption is used to establish mathematical relationships between pollutant concentrations in the different phases. But this assumption does not take transfer kinetics into account. However, laboratory tests show the equilibrium is established rapidly (eg. 24-28 hours between soil and interstitial water) (van den Berg, 1994, cited in the INERIS report, 2005b). This assumption is also conservative for past pollution because it does not consider the possible irreversibility of pollutant adsorption, particularly for past contamination events).

1.1.1.1. SITUATION WHERE THE SOLUBILITY LIMIT IS NOT REACHED

In this case, the concentrations in soil air, soil water and on soil particles are calculated from the following equations:

$$m_s = m_{ps} + m_{es} + m_{as}$$

Equation 1.1.1

where m_s: total mass of pollutant in the soil,

m_{ps}: mass of pollutant adsorbed to soil particles,

m_{es} : mass of pollutant dissolved in soil water,

m_{as} : mass of pollutant dissolved in soil air.

and $$m_s = MV_s \times V \times C_s$$

Equation 1.1.2

where MV_s: bulk soil density,

V: volume of soil considered,

C_s: concentration of pollutant in soil (expressed relative to the dry weight of soil).

$$m_{ps} = MV_{ps} \times V_{ps} \times C_{ps} = MV_{ps} \times V \times (1 - \theta - \alpha) \times C_{ps} = MV_s \times V \times C_{ps}$$ Equation 1.1.3

where MV_{ps}: density of soil particles,

V_{ps}: volume occupied by particles,

C_{ps}: concentration of pollutant adsorbed on particles,

θ: volume fraction occupied by soil water,

α: volume fraction occupied by soil air.

$$m_{es} = V_{es} \times C_{es} = V \times \theta \times C_{es}$$

Equation 1.1.4

where V_{es}: volume occupied by soil water,

C_{es}: concentration of pollutant in soil water.

$$m_{as} = V_{as} \times C_{as} = V \times \alpha \times C_{as}$$

Equation 1.1.5

where V_{as}: volume occupied by soil air,

C_{as}: concentration of pollutant in soil air.

If **the relationship between the concentration adsorbed on particles is linear** compared to the concentration dissolved in soil water (which does not take account of possible irreversibility of pollutant adsorption, particularly for past contamination events), it follows:

$$K_d = \frac{C_{ps}}{C_{es}}$$ *(Freundlich equation: $K_d = \frac{C_{ps}}{(C_e)^n}$ where n=1)*

Equation 1.1.6

where K_d: partition coefficient between soil particles and soil water.

Furthermore, the concentration in soil water and air are linked by the Henry constant, so that:

$$H' = \frac{C_{as}}{C_{es}}$$

Equation 1.1.7

where H': Henry constant is dimensionless:

$$H' = \frac{H}{R \times T_s}$$

<div align="right">Equation 1.1.8</div>

where H: Henry constant ($L^2.M.T^{-2}.Mol^{-1}$)

R: universal gas constant ($L^2.M.T^{-2}.K^{-1}.Mol^{-1}$)

T_s: soil temperature (K)

Hence, using equations 1.1.1 to 1.1.5:

$$MV_s \times V \times C_s = MV_s \times V \times C_{ps} + V \times \theta \times C_{es} + V \times \alpha \times C_{as}$$

<div align="right">Equation 1.1.9</div>

and from equations 1.1.6 to 1.1.9, it follows:

$$C_s = C_{ps} + \frac{\theta}{MV_s} \times C_{es} + \frac{\alpha}{MV_s} \times C_{as}$$

<div align="right">Equation 1.1.10</div>

$$C_{es} = C_s \times \frac{1}{\left(K_d + \dfrac{\theta}{MV_s} + \dfrac{\alpha \times H}{MV_s \times R \times T_s} \right)}$$

<div align="right">Equation 1.1.11</div>

$$C_{as} = C_s \times \frac{1}{\left(\dfrac{K_d \times R \times T_s}{H} + \dfrac{\theta \times R \times T_s}{H \times MV_s} + \dfrac{\alpha}{MV_s} \right)}$$

<div align="right">Equation 1.1.12</div>

and
$$C_{ps} = C_s \times \frac{1}{\left(1 + \dfrac{\theta}{MV_s \times K_d} + \dfrac{\alpha \times H}{MV_s \times R \times T_s \times K_d} \right)}$$

<div align="right">Equation 1.1.13</div>

Symbol	Parameters	Dimensions	Units	Status
C_{es}	Pollutant concentration in the soil water	$M.L^{-3}$	$mg.m^{-3}$	C or E
C_{as}	Pollutant concentration in the soil air	$M.L^{-3}$	$mg.m^{-3}$	C or E
C_{ps}	Pollutant concentration adsorbed on particles	$M.M^{-1}$	$mg.kg^{-1}$	C or E
C_s	Pollutant concentration in the soil (expressed in terms of soil dry weight)	$M.M^{-1}$	$mg.kg^{-1}$	C or E
K_d	Partition coefficient between soil particles and soil water	$L^3.M^{-1}$	$m^3.kg^{-1}$	C or E
MV_s	Bulk soil density	$M.L^{-3}$	$kg.m^{-3}$	E
α	Volume fraction occupied by soil air	-	-	E
θ	Volume fraction occupied by soil water	-	-	E
H	Henry constant	$L^2.M.T^{-2}.Mol^{-1}$	$Pa.m^3.mol^{-1}$	C or E
R	Universal gas constant	$L^2.M.T^{-2}.K^{-1}.Mol^{-1}$	$8.31\ J.K^{-1}.mol^{-1}$	I
T_s	Soil temperature	K	K	E

Comment:

1. C_s is generally expressed relative to dry weight (as the quantity of pollutant present in the different phases: m_s, divided by the weight of dry particles: MV_{ps} x V x (1-θ-α) or MV_s x V).

2. α, θ, K_d and T_s can vary with environmental conditions. Nonetheless, the frequency and impact of the variations considered should be sufficiently low

to be compatible with an equilibrium state being established between the different soil phases.

1.1.1.2. SITUATION WHERE THE SOLUBILITY LIMIT IS REACHED

In this case, there is an immiscible pollutant phase in the soil.

If the substance is pure, the solubility limit is reached when the concentration in the soil is C_{sL}, where:

$$C_{sL} = S \times \left(K_d + \frac{\theta}{MV_s} + \frac{\alpha \times H}{MV_s \times R \times T_s} \right)$$

Equation 1.1.14

and hence:

$$C_{es} = S$$

Equation 1.1.15

and

$$C_{as} = \frac{H}{R \times T_s} \times S$$

Equation 1.1.16

From the universal gas equation: $\dfrac{C_{as}}{1000 \times M} = \dfrac{P_{vap}}{R \times T_s}$

Equation 1.1.17

where M: molar mass of pollutant (the factor 1000 in the denominator takes account of the fact that the molar mass is traditionally expressed as g.mol^{-1} while the concentration in soil air is assumed to be given here as mg.m^{-3})

At saturation it can therefore also be stated:

$$C_{as} = \frac{P_{vap} \times M \times 1000}{R \times T_s}$$

Equation 1.1.18

Symbol	Parameters	Dimensions	Units	Status
C_{sL}	Pollutant concentration in the soil (expressed as soil dry weight) at the solubility limit	M.M^{-1}	mg.kg^{-1}	C
C_{es}	Pollutant concentration in the soil water	M.L^{-3}	mg.m^{-3}	C or E
C_{as}	Pollutant concentration in the soil air	M.L^{-3}	mg.m^{-3}	C or E
S	Solubility of the pollutant	M.L^{-3}	mg.m^{-3}	E
K_d	Partition coefficient between soil particles and soil water	L^3.M^{-1}	m^3.kg^{-1}	C or E
MV_s	Bulk soil density	M.L^{-3}	kg.m^{-3}	E
α	Volume fraction occupied by soil air	-	-	E
θ	Volume fraction occupied by soil water	-	-	E
P_{vap}	Vapour pressure of the pollutant	M.L^{-1}.T^{-2}	Pa	E
M	Molar mass of the pollutant	M.Mol^{-1}	g.mol^{-1}	E
H	Henry constant	L^2.M.T^{-2}.Mol^{-1}	Pa.m^3.mol^{-1}	C or E
R	Universal gas constant	L^2.M.T^{-2}.K^{-1}.Mol^{-1}	8.3143 J.K^{-1}.mol^{-1}	I
T_s	Soil temperature	K	K	E

If the substance is present in a mixture, Raoult's law leads to:

$$C_{sL,j} = x_j \times S \times \left(K_d + \frac{\theta}{MV_s} + \frac{\alpha \times H}{MV_s \times R \times T_s} \right)$$

Equation 1.1.19

$$C_{es,j} = x_j \times S$$

Equation 1.1.20

$$C_{as,j} = x_j \cdot \frac{P_{vap,j} \times M_j \times 1000}{R \times T_s}$$

Equation 1.1.21

where $x_j = \dfrac{C_{s,j}/M_j}{\sum\limits_j C_{s,j}/M_j}$

Equation 1.1.22

Symbol	Parameters	Dimensions	Units	Status
$C_{sL,j}$	Concentration of pollutant j in the soil (expressed in terms of soil dry weight) at the solubility limit	M.M^{-1}	mg.kg^{-1}	C
$C_{s,j}$	Concentration of pollutant j in the soil	M.M^{-1}	mg.kg^{-1}	C or E
$C_{es,j}$	Concentration of pollutant j in soil water	M.L^{-3}	mg.m^{-3}	C or E
$C_{as,j}$	Concentration of pollutant j in soil air	M.L^{-3}	mg.m^{-3}	C or E
S	Solubility of the pollutant	M.L^{-3}	mg.m^{-3}	E
R	Universal gas constant	L^2.M.T^{-2}.K^{-1}.Mol^{-1}	8.3143 J.K^{-1}.mol^{-1}	I
T_s	Soil temperature	K	K	E
$P_{vap,j}$	Vapour pressure of pollutant j	M.L^{-1}.T^{-2}	Pa	E
M_j	Molar mass of pollutant j	M.Mol^{-1}	g.mol^{-1}	E
x_j	Molar fraction of pollutant j in the mixture	-	-	C or E

Comment: These equations assume uniform distribution of the pollutant in the soil. In reality, the pollutant, which is often initially introduced as concentrated product, may be distributed non-uniformly in the soil (particularly as a result of its viscosity), leaving voids and zones of high concentrations. As a result, an immiscible phase can exist for pollutant quantities in the soil less than those determined using the above equations (INERIS, 2005b).

1.1.2. POLLUTANT CONCENTRATION IN THE SURFACE SOIL LAYER

The pollutant concentration in a soil layer at time t depends on the initial pollutant concentration and the quantities of pollutant introduced to this layer and lost by this layer in the interval to time t.

Loss mechanisms that can contribute to reducing the pollutant concentration in the soil are:

- leaching,
- volatilisation,
- degradation (biological and abiotic).

The soil layer located at the soil surface can also suffer losses due to:

- erosion by wind and water,
- runoff,
- root uptake by plants.

Because the impact of these loss mechanisms are difficult to quantify and the associated uncertainties are significant, these loss mechanisms are often neglected in health risk assessments, for reasons of simplification and caution. In the absence of inflow, the concentration in the soil is therefore considered as constant over time. Conversely, as long as there is pollutant inflow into the soil, if the loss phenomena referenced above are not considered, the estimated pollutant concentration in the soil increases. If inflows and losses are considered, the concentration in the soil can reach a steady state level. But this steady state level may not be reached before the end of the deposition period studied.

Section 1.1.2.2 focuses on estimating inflows. Methods of estimating losses are presented in section 1.1.2.3 and the expression for pollutant concentrations in soil attributable to the sources(s) of pollution studied over time is given in section 1.1.2.4.

As stated in section 3, sub-chronic and chronic risks are estimated from the average exposure of receptors over exposure periods (d_{exp}) ranging from a few days to several years. In certain cases, depending on the calculation tools used, it may be more practical for assessors to estimate average exposure over the period d_{exp} from average concentrations in the exposure media over this period, rather than estimate this exposure as the average of ad hoc exposure levels calculated at different time increments. If the average concentration in the media over period d_{exp} can be expressed in the form of an analytical expression, this approach avoids calculating concentrations and exposures for a large number of time increments. Nonetheless it assumes that the exposure parameters for the receptor can be considered as constant over the period considered. Thus section 1.1.2.5 gives the average pollutant concentration in the soil over a given period for different cases.

1.1.2.1. MASS BALANCE OF POLLUTANT IN THE SURFACE SOIL

The quantity of pollutant in the soil is calculated from the pollutant mass balance in the mass of soil considered.

Hence:

$$\frac{dm_s}{dt} = D_s \times S_s \times Z_s \times MV_s - \sum_i [FM_s]_i$$

Equation 1.1.23

Symbol	Parameters	Dimensions	Units	Status
m_s	Pollutant mass in the soil	M	mg	C or E
D_s	Pollutant inflow to the soil per unit time	$M.M^{-1}.T^{-1}$	$mg.kg^{-1}.s^{-1}$	C or E
$[FM_s]_i$	Pollutant mass lost by the soil through attenuation per unit time	$M.T^{-1}$	$mg.s^{-1}$	C or E
MV_s	Bulk soil density	$M.L^{-3}$	$kg.m^{-3}$	E
Z_s	Thickness of the soil layer where the pollutant accumulates	L	m	E
S_s	Surface area of the zone considered	L^2	m^2	E

Comment: Pollutant inflows to the soil and pollutant losses from the soil, presented below, only take account of local contamination sources (on and around the site), without considering ubiquitous man-made pollutant sources and the natural pedogeochemical background concentration. In general, the equations described in section 1.1.2 are therefore given to calculate quantities (m_s) and concentrations of pollutant in the soil attributable to pollution sources on and around the site (C_s), excluding background concentrations. To distinguish between attributable concentrations and total concentrations and to estimate total concentrations, refer to section 4.

1.1.2.2. INFLOWS TO SURFACE SOIL

1.1.2.2.1. ESTIMATING ATMOSPHERIC DEPOSITION TO THE SOIL

Inflows at the surface of the soil can be particulate and gaseous. In both cases, there is a dry fraction and a wet fraction.

Taking account of deposits on the soil when assessing health risks is relevant for semi-volatile (such as PCB) or non-volatile (such as metals) pollutants. For volatile pollutants (such as benzene), exposure by ingestion and dermal contact, arising from transfers from the air to the soil, are negligible compared to exposure by inhalation.

Deposits on the soil are either measured or estimated using an atmospheric dispersion model.

The measurement is generally made using total fallout collectors. There are also wet deposit collectors.

In atmospheric dispersion models, deposits are estimated from atmospheric concentrations. The calculation principles used in these models are presented in sections 1.1.2.2.1.1 and 1.1.2.2.1.2 below.

1.1.2.2.1.1. CALCULATION OF DRY DEPOSIT

The dry pollutant deposit onto the soil (defined per unit time and area) is proportional to the pollutant concentration in the air close to the soil:

$$D_{\sec} = v_d \times C_a(x, y, 0)$$

Equation 1.1.24

where C_a (x,y,0): pollutant concentration in the air at soil level,

v_d: deposition velocity.

The deposition velocity includes a diffusive component ($v_{d'}$) and a gravitational component (v_s).

Deposition by diffusion affects gas and particles. It is due to three phenomena:
- aerodynamic transport through the surface atmospheric layer, under the effect of turbulent movements,
- transport through the very thin layer of stagnant air located just above the soil under the surface layer. It is due to molecular diffusion (for gases) or to Brownian motion (for particles),
- absorption through the surface (for gases), adhesion at the surface (for particles).

Deposition by gravity is specific to particles.

In the absence of data on deposition velocities, the latter can be estimated as the inverse of a sum of several resistances.

For gases, deposition velocity is considered as the inverse of three resistances:

$$v_d = \frac{1}{r_a + r_b + r_s}$$

Equation 1.1.25

Where r_a: aerodynamic resistance,

r_b: resistance of the laminar sub-layer,

r_c: surface resistance.

These resistance terms depend on the pollutant, the nature of the surface and the wind speed.

For particles, deposition velocity is estimated depending on the models, either as:

$$v_d = \frac{1}{r_a + r_b + r_a \times r_b \times v_s}$$

Equation 1.1.26

(Seinfeld and Pandis, 1998)

where v_s: gravitational velocity,

or as:

$$v_d = \frac{v_s}{1 - \exp(-v_s / v_{d'})}$$

Equation 1.1.27

(Venkatram and Pleim, 1999)

where $v_{d'}$: diffusive velocity,

$$v_{d'} = \frac{1}{r_a + r_b}$$

Equation 1.1.28

1.1.2.2.1.2. CALCULATION OF WET DEPOSIT

Two main types of processes contribute to wet deposition: rainout (or *in-cloud scavenging,* and washout (or *below-cloud scavenging*). The first type relates to transformations that take place inside clouds; the second to incorporating pollutants in precipitation.

This complex set of reactions is generally modelled using a scavenging coefficient ($\Lambda_{\text{lessivage}}$), which when multiplied by the concentration in air (C_a) gives the quantity of pollutant captured in precipitation per unit time and area. Wet deposition of pollutant on the soil can be calculated by integrating this quantity over the vertical air column. By assuming the atmosphere is uniform over this column and capture is irreversible, it is defined by the following equation:

$$D_{humide} = \int_{0}^{\infty} \Lambda_{lessivage} \times C_a \, dz$$

Equation 1.1.29

The scavenging coefficient depends particularly on the pollutant, particle size distribution, precipitation rate and droplet size (Sportisse, 2007).

In the absence of data for $\Lambda_{\text{lessivage}}$, this parameter can be estimated using the following formula:

$$\Lambda_{lessivage} = A \times P^B$$

Equation 1.1.30

where P: precipitation,

A, B: coefficients.

1.1.2.2.1.3. Calculation of gaseous and particulate fractions

For pollutants able to exist in gaseous and particulate states at ambient temperature, atmospheric concentrations and deposits can be calculated, for both the gaseous fraction and the particulate fraction, by applying the particulate and gaseous fractions estimated at ambient temperature to the emission. This approach assumes a rapid fall in temperature of the pollutant flux after emission.

Pollutant fractions in particulate (F_p) and gaseous (F_g) phases are expressed as:

$$F_p = \frac{C_{ap}}{C_{ag} + C_{ap}} = \frac{K_{pg}}{1 + K_{pg}}$$

Equation 1.1.31

and $\quad F_g = 1 - F_p$

Equation 1.1.32

where C_{ag}: pollutant concentration in gaseous form in the air,

C_{ap}: pollutant concentration in particulate form in the air,

K_{pg}: particle/gas partition coefficient.

According to the Junge adsorption model (1977) (revised by PanKow, 1987):

$$K_{pg} = \frac{c \times S_T}{P_{vap,L}^{\circ}}$$

Equation 1.1.33

Hence $F_p = \dfrac{c \times S_T}{P_{vap,L}^{\circ} + c \times S_T}$

Equation 1.1.34

and $\quad F_g = \dfrac{P_{vap,L}^{\circ}}{P_{vap,L}^{\circ} + c \times S_T}$

Equation 1.1.35

Symbol	Parameters	Dimensions	Units	Status
F_g	Pollutant fraction in gaseous form	-	-	C or E
F_p	Pollutant fraction in particulate form	-	-	C or E
$P_{vap,L}$	Vapour pressure of the pollutant in liquid phase	$M.L^{-1}.T^{-2}$	atm	C or E
c	Junge constant	$M.T^{-2}$	1.7×10^{-4} atm.cm	I
S_T	Average surface area of aerosol particles per air volume	L^{-1}	$cm^2.cm^{-3}$	E

Bidleman (1988) gives different values for S_T depending on the environmental context.

Although Junge attributes a constant value to c, this parameter actually depends on the difference between the desorption heat of the particle surface and the vaporisation heat of the pollutant.

If the pollutant is solid at ambient temperature, its vapour pressure in liquid phase can be calculated from the following expression:

$$\ln(\frac{P^{\circ}_{vap,L}}{P^{\circ}_{vap,S}}) = \frac{\Delta S_f}{R} \times \frac{(T_m - T_a)}{T_a}$$

Equation 1.1.36

Symbol	Parameters	Dimensions	Units	Status
$P_{vap,L}$	Vapour pressure of the pollutant in liquid phase	$M.L^{-1}.T^{-2}$	atm	C or E
$P_{vap,S}$	Vapour pressure of the pollutant in solid phase	$M.L^{-1}.T^{-2}$	atm	E
$\Delta S_f/R$	Ratio of entropy of fusion over the universal gas constant	-	6.79 (-)	I
T_m	Melting temperature of the pollutant	K	K	E
T_a	Air temperature	K	K	E

Comments:

1. In its work to assess risks associated with dioxins, the US EPA (2004c) compared results supplied by the Junge equation with measurement data for polycyclic aromatic hydrocarbons (PAH), organochlorine pesticides, polychlorobiphenyls (PCB), polychlorodibenzodioxins (PCDD) and polychlorodibenzofurans (PCDF). Measurement and modelling results are very close for PAHs. For PCB and organochlorine pesticides, the model tends to overestimate the particulate fraction, but this overestimate is even greater for PCDD and PCDF (this test shows a percentage of TCDD and TCDF in particulate form in the air between 43 and 65% based on the model and between 11 and 18% from measurements). Nonetheless, given the problems associated with the sampling method in this evaluation work, the US EPA favoured using the results from modelling rather than those from measurement.

2. There are other approaches (particularly based on the octanol-air partition coefficient) that, according to certain authors (Harner et al, 1998), enable pollutant fractions in gaseous and particulate forms to be estimated more accurately. These alternative approaches have not been analysed nor yet used by INERIS and therefore are not presented here.

1.1.2.2.1.4. SUM OF ATMOSPHERIC POLLUTANT FLUX TO THE SOIL

The total pollutant flux to the soil equals the sum of gaseous and particulate flux.

Particle deposition may comprise a dry flux and a wet flux (particles leached by precipitation).

$$D_{ps} = D_{pss} + D_{phs}$$
Equation 1.1.37

Gas deposition may comprise a dry flux (diffusion) and a wet flux (leaching and dissolution of gases in water).

$$D_{gs} = D_{gss} + D_{ghs}$$
Equation 1.1.38

Symbol	Parameters	Dimensions	Units	Status
D_{ps}	Pollutant flux to the soil in particulate form	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
D_{pss}	Particulate pollutant flux to the soil in dry form	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	E
D_{phs}	Particulate pollutant flux to the soil in wet form	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	E
D_{gs}	Pollutant flux to the soil in gaseous form	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
D_{gss}	Gaseous pollutant flux to the soil in dry form	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	E
D_{ghs}	Gaseous pollutant flux to the soil in wet form	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	E

Comment: certain models do not provide wet and dry gaseous deposits. Simplified methods (not used by INERIS) exist to estimate them (cf. Whelpdale, 1982 or US EPA, 1998).

1.1.2.2.2. CALCULATION OF OTHER INFLOWS

In general, pollutant flux contributed to the soil can be estimated as the product of the quantity of matrix added (fertilisers, sludges) multiplied by the pollutant concentration in this matrix. Depending on the nature of this matrix, the pollutant may have a different bioavailability and mobility. This aspect must be considered when determining values attributed to the parameters of chemical substances (partition coefficient between particles and water in the soil, soil-plant transfer coefficient, etc.).

For deposition by irrigation, it can be stated:

$$D_{ir,s} = C_{e,ir} \times I_r$$
Equation 1.1.39

Symbol	Parameters	Dimensions	Units	Status
$D_{ir,s}$	Pollutant flux to the soil by irrigation	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
I_r	Irrigation	$L.T^{-1}$	$m.s^{-1}$	E
$C_{e,ir}$	Pollutant concentration in the irrigation water	$M.L^{-3}$	$mg.m^{-3}$	C or E

Comment: The soil can also be contaminated by a polluted groundwater and fluctuating movements of this groundwater level. The mechanism for contaminating the soil is not covered in this document.

1.1.2.2.3. CALCULATION OF TOTAL INFLOW TO THE SOIL

Pollutant inflow fluxes are assumed to be diluted in a soil zone of depth Z_s, hence:

$$D_s = \frac{\sum_i D_{i,s}}{MV_s \times Z_s}$$

Equation 1.1.40

As stated above, several soil layers are considered depending on the use of the zone and the transfer phenomenon studied (eg. to estimate the contamination of plants by root uptake from the soil, Z_s can be defined depending on the height of the root area development of the plants, whereas for estimating transfers and exposures by contact with surface soil, a very superficial layer of 1 or 2 cm can be taken into account if the soil is not worked or dug over regularly).

Symbol	Parameters	Dimensions	Units	Status
D_s	Total pollutant deposition to the soil	$M.M^{-1}.T^{-1}$	$mg.kg^{-1}.s^{-1}$	C or E
$D_{i,s}$	Pollutant flux i to the soil	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
MV_s	Bulk soil density	$M.L^{-3}$	$kg.m^{-3}$	E
Z_s	Thickness of the soil layer where the pollutant accumulates	L	m	E

Comment:

D_s is inversely proportional to Z_s. Overestimating Z_s therefore leads to underestimating D_s and vice-versa.

It must be emphasised here that while the definition of Z_s is based on agronomic conditions, this representation method remains conventionally-agreed and is not a physical representation of actual phenomena giving information about the pollutant gradient in soils. Where there is continuous deposition at the soil surface and in the absence of action to homogenise the soil, the soil concentration actually presents a negative gradient with the depth. The action of soil organisms (mice, earthworms, etc.) and ploughing tend to homogenise the pollutant concentration in the soil. However, ploughing the soil is an occasional activity repeated once or twice per year. Between two ploughings, if the deposit at the soil surface is significant compared to the average concentration in the ploughed soil layer, then the concentration will indeed demonstrate a negative gradient with depth.

1.1.2.3. LOSSES FROM THE SOIL

The pollutant concentration in the soil can be reduced over time by leaching, erosion, runoff, volatilisation or degradation phenomena.

These loss phenomena may be considered or disregarded when estimating pollutant concentrations in the soil.

Failure to consider them results in overestimating the pollutant concentration in the soil, which then tends to increase indefinitely with inflows. Conversely, taking them into account can result in underestimating the soil concentration (therefore the concentration of media contaminated from the soil and by

exposure). The impact of these phenomena is very variable and estimating them can be delicate.

The various loss or attenuation phenomena cited above can be considered in overall terms. After reviewing the literature, the US EPA (2004c) thus defined an overall loss coefficient k (such that $\sum[FM_s] = k \times m_s$) to represent the attenuation of dioxins in a soil layer of given depth.

The attenuation rate of a pollutant in a soil depends on the properties of the soil (pH, organic matter content, etc.), the characteristics of the pollutant or mixture of pollutants present (concentrations, etc.) and the configuration of the site (slope, plant coverage, etc.). It is therefore preferable to use an attenuation rate defined from site data (corresponding to the different loss mechanisms involved). The attenuation rate measured in the given soil layer is not necessarily representative for other conditions, so it is also necessary to be careful over the protocol for estimating this value.

But sometimes the pollutant quantity lost by a soil is estimated as the sum of the quantities lost due to each of the attenuation phenomena (cf. US EPA, 2005). If each of these quantities is estimated independently, without considering co-existence of the different phenomena, pollutant quantities lost can be overestimated (since the quantity of pollutant available for each phenomenon is overestimated).

Methods for estimating the impact of different attenuation phenomena on pollution in the soil are presented in the following sections. They employ parameters that can prove difficult to define and there may be a high degree of uncertainty associated with estimating them. Using these simple methods, **each attenuation phenomenon** is thus **considered independently from the others**.

Besides the assumptions given in sections relating to each of these mechanisms, the reader should refer to section 1.1.2.3.6 presenting limitations common to these different expressions and how to use them.

Comment: loss phenomena associated with root uptake of pollutants from the soil to plants are not considered. It will be noted that in some cases the transfer of pollutants from the soil to plants is compensated by the fact that one part of the plant can, after harvest, remain in place and be reincorporated into the soil or be consumed by animals, the faeces of which can also return to the soil.

1.1.2.3.1. LOSSES BY LEACHING

The mass of pollutant leaving the soil layer considered, per unit time, due to leaching is:

$$[FM_s]_l = R_{ech} \times S_s \times C_{es}$$

Equation 1.1.41

where C_{es}: concentration of pollutant in soil water,

S_s: soil area considered,

R_{ech}: leaching flux.

1. **If the pollutant concentration in the soil is below the limit of solubility and if multiphase equilibrium is reached**, equation 1.1.11 leads to:

$$[FM_s]_l = \frac{R_{ech} \times S_s}{K_d + \dfrac{\theta}{MV_s} + \dfrac{\alpha \times H}{MV_s \times R \times T_s}} \times C_s$$

Equation 1.1.42

where K_d: partition coefficient between soil particles and soil water,

θ: volume fraction occupied by soil water,

α: volume fraction occupied by soil air,

H: Henry constant,

R: universal gas constant,

T_s: soil temperature,

C_s: pollutant concentration in the soil,

MV_s: bulk soil density.

Furthermore, if $\alpha \times \dfrac{H}{R \times T_s} \prec\prec \theta + K_d \times MV_s$

(assumption by which the pollutant fraction present in the gaseous phase is negligible compared to the sum of pollutant fractions adsorbed on the particles and dissolved in the soil water), then:

$$[FM_s]_l = \frac{R_{ech} \times S_s}{K_d + \dfrac{\theta}{MV_s}} \times C_s$$

Equation 1.1.43

In this case, a leaching loss coefficient (k_l) can be defined such that:

$$[FM_s]_l = MV_s \times Z_s \times S_s \times k_l \times C_s$$

Equation 1.1.44

and $k_l = \dfrac{R_{ech}}{(MV_s \times K_d + \theta) \times Z_s}$

where Z_s: depth of the soil layer.

Equation 1.1.45

2. **If the solubility limit is reached**, the loss by leaching is not expressed as a function of the concentration in the soil (C_s).

According to section 1.1.1.2,

if the pollutant is in pure phase, then:

$$[FM_s]_l = R_{ech} \times S \times S_s$$

Equation 1.1.46

where S: solubility of the pollutant in water,

if the pollutant is present in a mixture, then:

$$[FM_s]_{l,j} = R_{ech} \times x_j \times S \times S_s$$

Equation 1.1.47

where x_j: molar fraction of pollutant j in the mixture

Symbol	Parameters	Dimensions	Units	Status
$[FM_s]_i$	Mass of pollutant leaving the soil layer by leaching per unit time	M.T^{-1}	mg.s^{-1}	C or E
k_l	Leaching loss coefficient	T^{-1}	s^{-1}	C or E
R_{ech}	Leaching flux	L.T^{-1}	m.s^{-1}	C or E
K_d	Partition coefficient between soil particles and soil water	L^3.M^{-1}	m^3.kg^{-1}	C or E
Z_s	Depth of soil layer	L	m	E
θ	Volume fraction occupied by soil water	-	-	E
MV_s	Bulk density of the soil layer	M.L^{-3}	kg.m^{-3}	E
S	Solubility of the pollutant in water	M.L^{-3}	mg.m^{-3}	E
x_j	Molar fraction of pollutant j in the mixture (cf. equation 1.1.22)	-	-	C or E

Comment: The residence time of water in the soil is a determining factor in reaching chemical equilibrium in the leached water. Also, expressions 1.1.41 and 1.1.42 can overestimate losses.

Expression for leaching flux

The leaching flux is calculated by performing a water balance for water inflows to the soil and water losses from the soil over a given period T.

The water balance in a soil is generally defined with a time increment (ΔT_i) of a day or even a decade. Hence:

$$R_{ech} = \frac{1}{\sum \Delta T_i} \times \max\left[(P + I_r - RO - E_T) \times \Delta T_i - (RU - R); 0\right] \qquad \text{Equation 1.1.48}$$

Symbol	Parameters	Dimensions	Units	Status
R_{ech}	Leaching flux	L.T^{-1}	m.s^{-1}	C or E
E_T	Evapotranspiration	L.T^{-1}	m.s^{-1}	E
I_r	Irrigation	L.T^{-1}	m.s^{-1}	E
P	Precipitation	L.T^{-1}	m.s^{-1}	E
RO	Runoff	L.T^{-1}	m.s^{-1}	E
RU	Available water holding capacity in the soil	L	m	E
R	Water reserve in the soil	L	m	E
ΔT_i	Time increment	T	s	E

The available water holding capacity RU equals the difference in water depth between the field capacity and the wilting point. RU depends on the soil type.

Comment:

If the leaching flux (R_{ech}) is estimated from annual data as in US EPA (2005) and if at the end of a year the available water storage capacity of the soil has been restored, it can be stated:

$$R_{ech} = P + I_r - RO - E_T \qquad \text{Equation 1.1.49}$$

Actual evapotranspiration over a site is calculated from the potential evapotranspiration. Potential evapotranspiration (evapotranspiration of a soil with grass and saturated with water) is given by METEOFRANCE or can be estimated using different methods (Thorthwaite, 1948; Penman, 1948). Actual evapotranspiration is calculated taking account of the available water in the soil over time, as well as plant cover and its phenological state (FAO, 1998).

1.1.2.3.2. LOSSES BY RUNOFF

Models, particularly HHRAP (US EPA, 2005), CalTOX (University of California, 1993, 1997) and SimpleBox (RIVM, 1996), include pollutant loss in the soil by runoff in the form:

$$[FM_s]_r = RO \times S_s \times C_{es}$$
Equation 1.1.50

where $[FM_s]_r$: pollutant mass lost by runoff per unit time,

C_{es}: concentration of pollutant in soil water,

S_s: soil area considered,

RO: runoff.

1. **If the pollutant concentration in the soil is below the limit of solubility and if multiphase equilibrium is reached**, equation 1.1.11 leads to:

$$[FM_s]_r = \frac{RO \times S_s}{K_d + \frac{\theta}{MV_s} + \frac{\alpha \times H}{MV_s \times R \times T_s}} \times C_s$$
Equation 1.1.51

where K_d: partition coefficient between soil particles and soil water,

θ: volume fraction occupied by soil water,

α: volume fraction occupied by soil air,

H: Henry constant,

R: universal gas constant,

T_s: soil temperature,

C_s: pollutant concentration in the soil,

MV_s: bulk soil density.

Furthermore, if $\alpha \times \dfrac{H}{R \times T_s} \prec\prec \theta + K_d \times MV_s$

(assumption by which the pollutant fraction present in the gaseous phase is negligible compared to the sum of pollutant fractions adsorbed on the particles and dissolved in the water), then:

$$[FM_s]_r = \frac{RO \times S_s}{K_d + \frac{\theta}{MV_s}} \times C_s$$
Equation 1.1.52

In the case, a runoff loss coefficient (k_r) can be defined such that:

$$[FM_s]_r = MV_s \times Z_s \times S_s \times k_r \times C_s$$
Equation 1.1.53

and
$$k_r = \frac{RO}{\theta \times Z_s \times \left(1 + \frac{MV \times K_d}{\theta}\right)}$$
Equation 1.1.54

where Z_s: depth of the soil layer.

2. **If the solubility limit is reached**, the loss by runoff is not expressed as a function of the pollutant concentration in the soil (C_s).

According to section 1.1.1.2,

if the pollutant is in pure phase, it is written similarly to equation 1.1.50:

$$[FM_s]_r = RO \times S \times S_s$$

Equation 1.1.55

where S: solubility of the pollutant in water,

and if the pollutant is present in an immiscible phase, it is written similarly to equation 1.1.50:

$$[FM_s]_{r,j} = RO \times x_j \times S \times S_s$$

Equation 1.1.56

where x_j: molar fraction of pollutant j in the mixture

Symbol	Parameters	Dimensions	Units	Status
$[FM_s]_r$	Pollutant mass lost by runoff per unit time	$M.T^{-1}$	$mg.s^{-1}$	C or E
k_r	Runoff loss coefficient	T^{-1}	s^{-1}	C or E
RO	Runoff	$L.T^{-1}$	$m.s^{-1}$	E
K_d	Partition coefficient between soil particles and soil water	$L^3.M^{-1}$	$m^3.kg^{-1}$	C or E
Z_s	Depth of soil layer	L	m	E
θ	Volume fraction occupied by soil water	-	-	E
MV_s	Bulk density of the soil layer considered	$M.L^{-3}$	$kg.m^{-3}$	E
S	Solubility of the pollutant in water	$M.L^{-3}$	$mg.m^{-3}$	E
x_j	Molar fraction of pollutant j in the mixture (cf. equation 1.1.22)	-	-	C or E

Comments:

1. Runoff can be estimated using empirical runoff coefficients (Chow, 1964). Average runoff is obtained by multiplying the coefficients by average precipitation.

   Runoff can also be estimated on a daily basis using the USDA Soil Conservation Service method. This method takes account of precipitation, soil type, hydrological conditions of the soil, type of cover and humidity of the soil. It is described in the US EPA report entitled 'A screening procedure for toxic and conventional pollutants in surface and ground water – Part I' (revised – 1985).

2. The equations above assume that:
   - the pollutant concentration in the soil layer is uniform,
   - all the water running off the soil is at equilibrium with the pollutant concentration in the soil. For kinetic reasons, using these equations for a contaminated plot tends to overestimate the loss of pollutant by runoff significantly. These relationships are more suitable for areas the size of a

watershed. They should therefore be reserved for this type of situation, taking account of the average pollutant concentration in the soil in this zone.

1.1.2.3.3. LOSSES BY EROSION

For contaminated sites, losses by erosion relate to the detachment and transport of particles from the soil in the zone studied to a deposition zone located outside the site under consideration. Erosion associated with the wind is distinct from that caused by water.

The mass of pollutant leaving the zone studied as a result of erosion per unit time is:

$$[FM_s]_{er} = X_e \times S_s \times C_s \qquad \text{Equation 1.1.57}$$

where C_s: pollutant concentration in the soil,

S_s: area considered,

X_e: soil mass detached and transported by water erosion per unit area and time.

For a pollutant at a concentration higher than the solubility limit, the benefit of considering erosion should be assessed in relation to the physical properties of the pollution. If it has a powdery nature, it will be appropriate to use relationship 1.1.57. On the other hand, detachment and transport of particles from the soil will be limited for pollution having a viscous nature.

An erosion loss coefficient (k_{er}) can be defined such that:

$$[FM_s]_{er} = MV_s \times Z_s \times S_s \times k_{er} \times C_s \qquad \text{Equation 1.1.58}$$

and $\quad k_{er} = \dfrac{X_e}{MV_s \times Z_s} \qquad \text{Equation 1.1.59}$

Symbol	Parameters	Dimensions	Units	Status
$[FM_s]_{er}$	Pollutant mass leaving the site by erosion per unit time	$M.T^{-1}$	$mg.s^{-1}$	C or E
k_{er}	Erosion loss coefficient	T^{-1}	s^{-1}	C or E
X_e	Soil mass detached and transported by water erosion per unit area and time	$M.L^{-2}.T^{-1}$	$kg.m^{-2}.s^{-1}$	C or E
MV_s	Bulk density of the soil layer	$M.L^{-3}$	$kg.m^{-3}$	E
S_s	Surface area of the zone considered	L^2	m^2	E
Z_s	Depth of soil layer	L	m	E

1.1.2.3.3.1. CALCULATING THE SOIL MASS DETACHED AND TRANSPORTED BY WATER EROSION

Erosion can be due to the action of wind and water.

The pollutant quantity exported from the soil in the air is actually due to the mechanical effects of the wind and vehicle passage. The quantity resuspended by wind action can be estimated from the emission flux of inhalable particles J_{part_10pm}, given by the empirical equation from Cowherd et al. (presented in

section 1.2.1). Cowherd et al. also give an empirical relationship to estimate the flux of particles resuspended by vehicles travelling on unsurfaced roads. Pollutant losses by the soil associated with the effects of the wind are not generally considered in multimedia models and INERIS has never considered them before. In fact, there is a great deal of uncertainty over the quantity actually removed from the site by atmospheric dispersion. CalTOX (University of California, 1993, 1997), one of the rare models to consider resuspension of soil particles in the air, assumes that the quantity of particles resuspended from the soil equals the quantity depositing on the soil.

In France, the main erosion mechanism is water erosion (however, in coastal areas, wind erosion can be significant) (ADEME et al., 2001).

Losses associated with water erosion can be expressed from the Universal Soil Loss Equation (USLE), which gives the **mean soil mass lost over the long term** (annual or seasonal average) at local scale. It is worth noting that this equation does not estimate soil losses associated with specific storm events.

According to the Universal Soil Loss Equation (ADEME et al, 2001):

$$X_e = 3,17.10^{-9} * R_f * K_f * C_f * P_f * L_f * S_f$$
Equation 1.1.60

where 3.17x10⁻⁹: conversion factor from tonnes per hectare per year to kilograms per square metre per second;

R_f: rainfall erosivity coefficient. R_f represents the influence of precipitation on erosion. This factor is based on the frequency and intensity of rainfall. In France, R_f can vary by almost two orders of magnitude. The Pihan map (1986) reproduced in the ADEME et al. document provides estimates of values by region;

K_f: erodibility coefficient of soils. K_f reflects the influence of soil properties on erosion. This factor takes account of soil cohesion and its resistance to dispersal and transport. According to ADEME et al., '*erodibility is very high for fine sands and relatively inflexible loams. It decreases as the proportion of clay and/or organic matter increases*'. Erodibility can be defined from charts depending on the content of sand, loam or organic matter, depending on the structure of the soil and its permeability. These charts are available in the ADEME et al. document;

C_f: factor taking account of the surface condition of the soil. C_f takes account of the surface condition of the soil and is defined compared to a standard condition (worked fallow soil). A value of 1 corresponds to bare soil, while a value of 0.1 or less will be assigned to soil covered with vegetation. For gardening crops, the US EPA (1998) recommends values between 0.1 and 0.7;

P_f: factor taking account of antierosive improvements to the land. Where there is no specific provision to reduce erosion, P_f should be assigned a value of 1. Lower values are used for specific improvements;

S_f: slope inclination coefficient;

L_f: slope length coefficient.

Wischmeier et al. (1978) proposes a table to estimate the product of coefficients L_f and S_f. But these parameters can also be estimated using the following relationships:

$$L_f = \frac{\sqrt{3.28*l}}{100}$$

Equation 1.1.61

$$S_f = 0.76 + 0.53*p + 0.076*p^2$$

Equation 1.1.62

where l: length of the slope (m)

and p: inclination of the slope (%).

Symbol	Parameters	Dimensions	Units	Status
X_e	Soil mass detached and transported by water erosion per unit area and time	$M.L^{-2}.T^{-1}$	$kg.m^{-2}.s^{-1}$	C or E
L_f	Slope length coefficient	-	-	C or E
S_f	Slope inclination coefficient	-	-	C or E
R_f	Rainfall erosivity coefficient	T^{-1}	yr^{-1}	E
K_f	Soils erodibility coefficient	$M.L^{-2}$	$tonne.ha^{-1}$	E
C_f	Soil surface condition coefficient	-	-	E
P_f	Antierosive improvement coefficient	-	-	E

1.1.2.3.3.2. COMMENTS ABOUT ESTIMATING LOSSES BY EROSION

The quantity of pollutant lost from the soil by erosion is estimated differently by the US EPA. According to documents from 1998 and 2005, it should be stated:

$$[FM_s]_{er} = X_e \times SD \times ER \times S_s \times C_{ps}$$

Equation 1.1.63

where $[FM_s]_{er}$: pollutant mass lost by erosion per unit time,

X_e: soil mass detached and transported by water erosion per unit area and time,

C_{ps}: pollutant concentration on soil particles,

ER: enrichment ratio,

SD: ratio between the mass of material transported downstream of the contaminated zone and the quantity eroded.

To estimate X_e, the US EPA recommends, as above, using the Universal Soil Loss Equation.

On the other hand, the US EPA introduces two new terms to estimate pollutant loss from the soil:

- enrichment ratio (ER). This factor takes account of the fact that these are the lightest particles (with a higher surface area to volume ratio and organic matter content) that are most easily eroded, and that these particles have higher pollutant concentrations than the soil *in situ*. This factor can therefore also be introduced into equations 1.1.57 and 1.1.59. However, without measurements, assigning values to this parameter remains difficult. Thus, the US EPA only proposes default values, independent of soil type, even if the expected values for this parameter are higher for sandy soils than for loam or silt soils (US EPA, 1998);

- the 'sediment delivery ratio' (SD). This factor is used to take account of the fact that, for a given area, a proportion of soil particles detached and transported by erosion are redeposited over the same area. Applying this parameter, defined from work by Vanoni (1975) to different watersheds, appears appropriate for relatively large areas, such as a watershed. For a plot, the Universal Soil Loss Equation can be used to estimate the quantity of particles that are detached and displaced outside the plot: using the SD ratio does not therefore seem necessary.

In addition, it is worth noting that the US EPA only considers the pollution present on the soil particles. It does not consider the pollutant in the aqueous fraction (the gas fraction can effectively be considered as negligible). For a good number of the pollutants studies in risk assessments (pollutants with high affinity for particles), omitting the aqueous fraction is not noticeable. But, if we want to generalise the relationship defining the quantity of pollutant lost from the soil by erosion, it appears preferable to use the pollutant concentration in the soil (C_s), rather than the fraction adsorbed on particles, because it can be assumed that the water surrounding the particles is in localised equilibrium with them.

Finally, as part of risk assessments associated with incinerator fallout, the US EPA (2005) recommends assigning a value 0 to the erosion loss coefficient, considering that over a given area the quantity of soil lost to the downstream zone is compensated by the quantity of soil arriving from the upstream zone. Ultimately, the definition for the quantity of soil lost by erosion should therefore take account of the site configuration and contamination level upstream of the site:

- if the zone upstream of the area studied is not contaminated by the source or sources studied (excluding the background concentration of contamination), equation 1.1.59 can be used to define a net erosion loss coefficient (k_{er}) for the study area;

- for a plot upstream of the zone studied with the same surface area, the same characteristics (identical quantity of sol lost) and the same contamination level, erosion will have no effect on contamination of the soil in the study zone and the net erosion loss coefficient (k_{er}) will be zero;

- for a plot upstream of the zone studied having a different concentration level C_s^e (excluding the background concentration of contamination), erosion will have a diluting or concentrating effect. Equation 1.1.59 can no longer be used and the pollutant concentration in the soil (C_s) attributable to the source studied cannot be estimated using equations 1.1.72 and 1.1.74. Equations 1.1.76 and 1.1.77, giving the mass and concentration of pollutant in the soil layer, respectively, should be used, where:

$$\left[FM_s \right]_{er} = S_s \times X_e \times (C_s - C_s^e)$$

<div align="right">Equation 1.1.64</div>

The pollutant concentration in the soil upstream of the watershed (C_s^e) will be estimated before C_s.

Equation 1.1.64 assumes that the plot located upstream has the same surface area and same characteristics as that studied. If not, the quantity of soil contributed by the plot located upstream must be evaluated using the surface area and quantity X_e specific to this plot. For large surface areas, using the SD factor (sediment delivery ratio) may become appropriate (cf. estimation method in section 1.5.2.1.2.1).

1.1.2.3.4. LOSSES BY VOLATILISATION

Reduced concentration in the soil by volatilisation only affects organic substances.

In equation 1.1.23 expressing the mass balance of pollutant in the surface soil, the transfer flow from the atmosphere to the soil is considered by estimating atmospheric deposition. In this equation, term for loss by volatilisation $\left[FM_s\right]_v$ therefore represents the transfer flow from the soil to the atmospheric compartment.

For a soil source, this flux can be estimated using the Jury et al. model (1990).

A simplified expression of this model is obtained when **diffusion is considered as the only phenomenon for transfer into the soil**. In this case, it can be stated:

$$\frac{\partial C_s}{\partial t} = DU_a \times \frac{\partial^2 C_s}{\partial z^2}$$

Equation 1.1.65

where C_s: pollutant concentration in the soil,

z: distance from the soil surface,

DU_a: multiphase diffusion coefficient in the soil layer studied (expressed from the concentration in soil air),

$$DU_a = \frac{D_e \times \dfrac{\theta^{\frac{10}{3}}}{n^2}}{H'} + D_a \times \frac{\alpha^{\frac{10}{3}}}{n^2}$$

Equation 1.1.66

where D_e: diffusion coefficient in water,

H': Henry constant (expressed in dimensionless form),

θ: volume fraction occupied by soil water,

α: volume fraction occupied by soil air,

n: soil porosity (n=α+θ).

The origin of equation 1.1.66 is presented in section 1.2.2.1.3.

For a soil layer with a uniform pollutant concentration $C_s(0)$, at the initial instant, from the surface (z=0) to a depth H_0 and zero concentration in the air, solving equation 1.1.65 gives an emission flux:

$$[FM_s(t)]_v = MV_s \times C_s(0) \times S_s \times \sqrt{\frac{DU_a}{\pi \times \left(\dfrac{K_d \times MV_s}{H'} + \dfrac{\theta}{H'} + \alpha\right) \times t}}$$

$$\times \left(1 - \exp^{-\dfrac{H_o{}^2 \times \left(\frac{K_d \times MV_s}{H'} + \frac{\theta}{H'} + \alpha\right)}{4 \times DU_a \times t}} \right) \qquad \text{Equation 1.1.67}$$

(Initial conditions: $C_s = C_s(0)$ at $t=0$, $C_s = 0$ for $t=0$ and $z > H_0$, $C_s = 0$ for $t > 0$ and $z=0$).

This equation also assumes an **isotropic soil layer**, a **pollutant concentration in the soil less than the solubility limit** and **maintaining the multiphase equilibrium.** Furthermore, **the effect of the stagnant layer of air at the soil surface is neglected**.

When there are several contaminated soil layers with different properties or if the polluted soil layer, thickness H_0, is covered by an uncontaminated thickness of soil, depth L, the pollutant flux lost by volatilisation can be estimated using the principle of superposition. In this latter case, it can be stated:

$$[FM_s(t)]_v = [FM_s(t)]_{v, H_0 + L} - [FM_s(t)]_{v, L} \qquad \text{Equation 1.1.68}$$

$$[FM_s(t)]_v = MV_s \times C_s(0) \times S_s \times \sqrt{\frac{DU_a}{\pi \times \left(\dfrac{K_d \times MV_s}{H'} + \dfrac{\theta}{H'} + \alpha\right) \times t}}$$

hence

$$\times \left(\exp^{-\dfrac{L^2 \times \left(\frac{K_d \times MV_s}{H'} + \frac{\theta}{H'} + \alpha\right)}{4 \times DU_a \times t}} - \exp^{-\dfrac{(H_o + L)^2 \times \left(\frac{K_d \times MV_s}{H'} + \frac{\theta}{H'} + \alpha\right)}{4 \times DU_a \times t}} \right) \qquad \text{Equation 1.1.69}$$

Symbol	Parameters	Dimensions	Units	Status
$[FM_s(t)]_v$	Transfer flow of a pollutant source in the soil towards the atmospheric compartment, by volatilisation at time t	$M.T^{-1}$	$mg.s^{-1}$	C or E
$C_s(0)$	Pollutant concentration in the contaminated soil layer, depth H_0 at the initial instant	$M.M^{-1}$	$mg.kg^{-1}$	E
K_d	Partition coefficient between soil particles and soil water	$L^3.M^{-1}$	$m^3.kg^{-1}$	C or E
DU_a	Multiphase diffusion coefficient in the soil layer (expressed from the concentration in soil air)	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
D_e	Diffusion coefficient of the pollutant in water	$L^2.T^{-1}$	$m^2.s^{-1}$	E
D_a	Diffusion coefficient of the pollutant in air	$L^2.T^{-1}$	$m^2.s^{-1}$	E
d_a	Height of air boundary layer above the soil	L	m	E
H'	Henry constant in dimensionless form ($H'=\dfrac{H}{R \times T_s}$)	-	-	C or E
n	Soil porosity (volume fraction): n=α+θ	-	-	C or E
θ	Volume fraction occupied by water in the soil	-	-	E
α	Volume fraction occupied by soil air	-	-	E
H_o	Thickness of the contaminated soil layer at the initial instant	L	m	E
L	Thickness of the uncontaminated soil layer above the contaminated later at the initial instant	L	m	E
S_s	Surface area of the zone considered	L^2	m^2	E
MV_s	Bulk density of the soil layer	$M.L^{-3}$	$kg.m^{-3}$	E

Comments:

1. The expressions presented in this section are applicable for a pollutant source enclosed in soil layer Z_s. They are not suitable for estimating the transfer flow for substances deposited at the soil surface into the atmosphere for an industrial facility in operation. In fact, they relate to a **finite quantity of pollutant initially present in the soil** and **not a continuous inflow** and is expressed as a function of the concentration in the soil at instant 0.

   On the other hand, after the facility stops operating, the pollutant deposited and present in the soil can be considered as a soil source, and it is possible to use the expressions above, with the concentration calculated in the soil layer at this moment.

2. Furthermore, the mass of pollutant lost by volatilisation depends on the depth of the polluted zone (H_0), therefore there is no point in calculating a mass balance for the layer in question Z_s using equation 1.1.67 or 1.1.69 (and they should not be used to calculate the pollutant concentration remaining in the soil over time) if the pollutant source extends below Z_s.

3. Section 1.2.2 presents other expressions (1.2.25, 1.2.31) to estimate the (net) emission flux from the soil. These expressions are based firstly on the assumption of a zero pollutant gradient in the soil, which assumes steady state conditions and a stationary source, and secondly on the assumption of constant pollutant diffusion through a soil layer of depth L. These assumptions are not suitable for estimating the reduction in the quantity of pollutant in a soil over time: they can lead to overestimating pollutant losses from the soil and underestimating the remaining pollutant concentration in the soil significantly.

1.1.2.3.5. LOSSES BY DEGRADATION

Losses by degradation can be associated with biological (due to microbial agents) or abiotic (by hydrolysis, photolysis, oxidation, etc....) phenomena.

Numerous models assume that losses by degradation follow 1st order kinetics. However, for example in the presence of an enzyme or a catalyst, degradation reactions tend rather to follow 2nd order kinetics.

Despite this, assuming 1st order kinetics is often considered acceptable for low pollutant concentrations. Certain models (such as MEPAS (Streile et al., 1996)) also use this assumption for concentrations above the solubility limit.

Following assumed 1st order kinetics, it can be stated:

$$[FM_s]_d = MV_s \times Z_s \times S_s \times k_{deg} \times C_s$$
Equation 1.1.70

Symbol	Parameters	Dimensions	Units	Status
$[FM_s]_d$	Pollutant mass lost by degradation per unit time	M.T^{-1}	mg.s^{-1}	C or E
k_{deg}	Degradation loss coefficient	T^{-1}	s^{-1}	C or E
C_s	Pollutant concentration in the soil	M.M^{-1}	mg.kg^{-1}	C or E

1.1.2.3.6. COMMON LIMITS FOR CONSIDERING DIFFERENT ATTENUATION PHENOMENA AND CONDITIONS FOR USING THEIR MATHEMATICAL EXPRESSIONS

Approaches developed to estimate pollutant losses from the soil are simplified approaches.

Calculating the pollutant concentration in mobile phases (soil air and water) performed in sections 1.1.2.3.1, 1.1.2.3.2 and 1.1.2.3.4 are based on comparing the pollutant concentration attributable to local sources with the corresponding concentration at the solubility limit (C_{sL} cf. section 1.1.1.2), without considering the background concentration. If the total pollutant concentration in the soil is greater than C_{sL}, then the pollutant proportion associated with local contamination sources in loss fluxes by leaching, runoff and volatilisation can be overestimated (because the background pollutant concentration, even if less mobile, can contribute to the concentration in mobile phases in the soil, while losses are limited by solubility of the substance).

But, in parallel, if the residence time for water in the soil is too short, the concentration in soil water is overestimated, as are losses by leaching and runoff.

Ref: DRC-14-141968-04378A

It must also be remembered that the variability of partition coefficients between particles and water in the soil (K_d) is significant and that uncertainty about this parameter and concentrations calculated from this parameter can be significant (at least an order of magnitude). In the case of a pollutant adsorbed onto particles from combustion, for example, the partition coefficient between particles and water in the soil, which affects pollutant fractions in the water and air (and available to be transferred by leaching, runoff and volatilisation) may be different, particularly greater, from those listed for soils. Underestimating K_d results in overestimating pollutant quantities lost and underestimating the concentration remaining in the soil.

The expressions presented above are also based on assumptions about the uniformity of soil properties and the pollutant concentration in the layer considered. Even if there are concentration differences over a small thickness, this assumption of uniform concentration is normally permitted for the surface soil layer considered when estimating exposure by direct contact (soil ingestion, dermal contact with the soil). The soil layer used by cultivated plants can be turned over between one and three times per year. The rest of the time and in other cases, the concentration in the soil has a negative gradient dependent on depth, when there is pollutant inflow at the surface. In this way, from the expressions developed above, losses by erosion and runoff can be underestimated and losses by leaching can be overestimated for the soil layer considered, if there is inflow at the surface. For a soil source and without inflow at the surface, losses by runoff and erosion can conversely be overestimated. Calculations of losses should actually be based on the pollutant concentration at the top of the soil layer for erosion and runoff, and on the concentration at the bottom of this layer for leaching. The impact of these approximations depends on each case, site conditions, the parameters used and the mobility of pollutants in the soil.

Underestimating Z_s can also lead to overestimating loss coefficients by leaching (k_l), runoff (k_r) and erosion (k_{er}).

Furthermore, as previously stated, calculating pollutant quantities lost from the soil due to the different phenomena occurring at the same time, using expressions defined independently, leads to overestimating losses. For example, the expression for losses by volatilisation for a soil source, expressed from the initial concentration of pollutant in the soil, is defined by assuming that diffusion is the only transfer mechanism likely to reduce the pollution in the soil. As previously stated, it is therefore preferable to estimate the simultaneous impact of the different attenuation mechanisms, for example by using an overall loss coefficient (k). Insofar as one phenomenon often tends to have a more significant impact that the others, another solution to avoid this overestimation pitfall is to identify the phenomenon that contributes most to attenuating the pollutant, then to select only this phenomenon when calculating the pollutant concentration in the soil over time.

In the end, erosion, runoff and photodegradation are the phenomena that affect the very first centimetres of soil from the soil surface, while leaching and volatilisation can affect the entire section of unsaturated soil. Depending on the soil depth considered, taking account of certain attenuation phenomena can therefore be more appropriate than for others.

Given these limits, in risk assessments intended to confirm the management measures adopted to assure an acceptable level of risk, INERIS only uses these equations for pollutant loss from the soil in the uncertainty assessment step to analyse the scale of possible variations in concentrations in the soil (initially calculated without considering attenuation phenomena) and for testing the resulting impact on exposures and risk.

1.1.2.4. CALCULATING THE CONCENTRATION IN THE SURFACE SOIL LAYER OVER TIME T

As stated in section 1.1.2.1, the expressions developed in this and the following sections are given to calculate pollutant concentrations in the soil attributable to different local contamination sources (on and around the site), without considering inflows to the soil corresponding to ubiquitous man-made pollutant sources and the natural pedogeochemical background concentration. According to this approach, the total pollutant concentration in the soil is obtained by adding the background concentration to the concentration calculated from the different local contamination sources (cf. section 4).

1. When pollutant masses lost by the soil due to attenuation phenomena are proportional to the concentration in the soil (losses by leaching and runoff, if the solubility limit of the pollutant is not reached, and loss by erosion), equation 1.1.23 for mass balance of pollutant in the soil layer can be re-written using the pollutant concentration in the soil. Hence:

$$\frac{dC_s}{dt} = D_s - C_s \times \sum_i k_i$$

Equation 1.1.71

where D_s: pollutant inflow to the soil by the contamination source or sources studied (sources on or around the site),

C_s: pollutant concentration in the soil,

k_i: loss coefficient for pollutant in the soil by attenuation phenomenon i.

Integrating equation 1.1.71, over time intervals (Δt) where the inflow to the soil and losses do not vary, gives:

$$C_s(t) = \frac{D_s}{\sum_i k_i} \times (1 - e^{-\sum_i k_i \times \Delta t}) + C_s(t - \Delta t) \times e^{-\sum_i k_i \times \Delta t}$$

Equation 1.1.72

$$\text{If } \sum_i k_i = 0, \ C_s(t) = D_s \times \Delta t + C_s(t - \Delta t)$$

Equation 1.1.73

If, over the entire period considered, inflow to the soil by the contamination source studied and loss coefficients do not vary, then:

$$C_s(t) = \frac{D_s}{\sum_i k_i} \times (1 - e^{-\sum_i k_i \times t}) + C_s(0) \times e^{-\sum_i k_i \times t}$$

Equation 1.1.74

$$\text{if } \sum_i k_i = 0, \ C_s(t) = D_s \times t + C_s(0)$$

Equation 1.1.75

Symbol	Parameters	Dimensions	Units	Status
$C_s(t)$	Pollutant concentration in the soil at time t	$M.M^{-1}$	$mg.kg^{-1}$	C or E
D_s	Inflow to the soil by the contamination source or sources studied (sources on or around the site)	$M.M^{-1}.T^{-1}$	$mg.kg^{-1}.s^{-1}$	C or E
k_i	Loss coefficient by attenuation phenomenon i	T^{-1}	s^{-1}	C or E
$C_s(0)$	Pollutant concentration in the soil at time t=0 (excluding background concentration)	$M.M^{-1}$	$mg.kg^{-1}$	C or E

<u>Comment</u>: In the case of a soil source and with no pollutant inflow from this source, the equations developed in this section apply with $D_s=0$.

2. When pollutant masses lost by the soil due to attenuation phenomena i are independent of the pollutant concentration in the soil (eg. when the solubility limit is reached), integrating equation 1.1.23 over time intervals (Δt) where the inflow to the soil and losses do not vary, gives:

$$m_s(t) = \left(D_s \times S_s \times Z_s \times MV_s - \sum_i \left[FM_s \right]_i \right) \times \Delta t + m_s(t - \Delta t) \qquad \text{Equation 1.1.76}$$

and
$$C_s(t) = \left(D_s - \frac{\sum_i \left[FM_s \right]_i}{S_s \times Z_s \times MV_s} \right) \times \Delta t + C_s(t - \Delta t) \qquad \text{Equation 1.1.77}$$

If the pollutant is in pure phase, as long as the environmental parameters defining losses by leaching, runoff and erosion and the degradation loss coefficient are constant, $\sum_{i \neq v} \left[FM_s \right]_i$ is constant. On the other hand, if the pollutant is in a mixture, $\sum_{i \neq v} \left[FM_s \right]_i$ varies with x_j (molar fraction of pollutant j in the mixture). This molar fraction can vary with time. In this case, a sufficiently-small time increment should be chosen and x_j should be recalculated for each time increment.

Symbol	Parameters	Dimensions	Units	Status
$m_s(t)$	Pollutant mass in the soil at time t	M	mg	C or E
$C_s(t)$	Pollutant concentration in the soil at time t	M.M^{-1}	mg.kg^{-1}	C or E
$\sum_i \left[FM_s \right]_i$	Sum of pollutant masses lost through attenuation phenomena per unit time	M.T^{-1}	mg.s^{-1}	C or E
D_s	Inflow to the soil by the contamination source or sources studied (local sources on or around the site)	M.M^{-1}.T^{-1}	mg.kg^{-1}.s^{-1}	C or E
MV_s	Bulk density of the layer considered	M.L^{-3}	kg.m^{-3}	E
S_s	Surface area of the zone considered	L²	m²	E
Z_s	Depth of soil layer considered	L	m	E

1.1.2.5. CALCULATING THE AVERAGE CONCENTRATION IN THE SOIL OVER THE EXPOSURE PERIOD

The average pollutant concentration in the soil over the exposure period (d_{exp}), from T_1 to T_2, can be calculated from the concentration in the soil over different time intervals (Δt_i):

$$\overline{C}_S (d_{exp}) = \frac{1}{T_2 - T_1} \times \sum_{i=1}^{n} \left[C_s(t_i) \times \Delta t_i \right]$$

Equation 1.1.78

where i: iteration number between 1 and n,

and
$$\sum_{i=1}^{n} \Delta t_i = T_2 - T_1$$

Symbol	Parameters	Dimensions	Units	Status
$\overline{C}_S (d_{exp})$	Average pollutant concentration in the soil during exposure period d_{exp}	M.M^{-1}	mg.kg^{-1}	C or E
d_{exp}	Duration of the exposure period considered: $d_{exp} = T_2 - T_1$	T	d	C
T_1	Beginning of the exposure period	T	d	E
T_2	End of the exposure period	T	d	E
$C_s(t_i)$	Concentration in the soil at time t_i	M.M^{-1}	mg.kg^{-1}	C or E

If the inflows and losses experienced by the soil do not vary over time (which is not true, for example, for transfer flow from the soil to the air defined as a function of time by expressions 1.1.68 and 1.1.69), an analytical expressions can be defined to calculate the average pollutant concentration in the soil over this period.

Ref: DRC-14-141968-04378A

To evaluate exposure associated with deposits on the soil of a facility emitting pollutants, two cases are distinguished and presented in the following sections:

- where the exposure period finishes before the end of the period of pollutant inflow into the soil by the source studied (section 1.1.2.5.1),

- where the exposure period finishes after the period of pollutant inflow into the soil by the source studied (section 1.1.2.5.2).

1.1.2.5.1. CASE FOR CONSTANT PARAMETERS WITH AN EXPOSURE PERIOD FINISHING BEFORE THE END OF EMISSIONS

1. **If the solubility limit of the pollutant in the soil water is not reached** and if the exposure period begins at the same time or after the start of pollutant inflow into the soil by the source studied, the average concentration in the soil during the exposure period from T_1 to T_2 is obtained by integrating equation 1.1.74:

or
$$\overline{C}_s(d_{exp}) = \frac{1}{T_2' - T_1'} \int_{T_1'}^{T_2'} \left[\frac{D_s}{\sum_i k_i} \times (1 - e^{-\sum_i k_i \times t}) + C_s(0) \times e^{-\sum_i k_i \times t} \right] dt \qquad \text{Equation 1.1.79}$$

hence

$$\overline{C}_s(d_{exp}) = \frac{D_s}{\sum_i k_i} + \left(\frac{D_s}{\left(\sum_i k_i\right)^2 \times (T_2' - T_1')} - \frac{C_s(0)}{\left(\sum_i k_i\right) \times (T_2' - T_1')} \right) \times \left(e^{-T_2' \times \sum_i k_i} - e^{-T_1' \times \sum_i k_i} \right)$$

Equation 1.1.80

where $C_s(0)$: concentration in the soil attributable to the pollution when t=0 (instant 0 has to be fixed between the beginning of emissions and the beginning of exposure).

If $\sum_i k_i = 0$, then $\overline{C}_s(d_{exp}) = \frac{1}{T_2' - T_1'} \int_{T_1'}^{T_2'} [D_s \times t + C_s(0)] dt$ \qquad Equation 1.1.81

And $\overline{C}_s(d_{exp}) = \frac{D_s}{2} \times (T_2' + T_1') + C_s(0)$ \qquad Equation 1.1.82

Symbol	Parameters	Dimensions	Units	Status
$\overline{C}_s(d_{exp})$	Average pollutant concentration in the soil during exposure period d_{exp}	M.M⁻¹	mg.kg⁻¹	C or E
D_s	Inflow to the soil by the contamination source or sources studied (local sources on and around the site)	M.M⁻¹.T⁻¹	mg.kg⁻¹.s⁻¹	C or E
k_i	Loss coefficient by attenuation phenomenon i	T⁻¹	s⁻¹	C or E
T_1'	Beginning of the exposure period¥	T	s	E
T_2'	End of the exposure period¥	T	s	E
$C_s(0)$	Concentration in the soil at time t=0 excluding background concentration (instant 0 is fixed between the beginning of emissions and the beginning of exposure),	M.M⁻¹	mg.kg⁻¹	C or E

¥: In expressions 1.1.79 to 1.1.82, the start and end dates for exposure must be converted to seconds.

2. **If the pollutant concentration in the soil is greater than the solubility limit** and if the exposure period starts at the same moment or after the beginning of pollutant inflow into the soil from the source studied, an analytical expression can also be calculated. This expression is of type:

$$\bar{C}_s(d_{\exp}) = \frac{1}{T_2^{'} - T_1^{'}} \times \int_{T_1^{'}}^{T_2^{'}} \left(D_s - \frac{\sum_i [FM_s]_i}{S_s \times Z_s \times MV_s} \right) \times t \times dt + C_s(0) \qquad \text{Equation 1.1.83}$$

$$\bar{C}_s(d_{\exp}) = \frac{1}{2} \times \left(D_s - \frac{\sum_i [FM_s]_i}{S_s \times Z_s \times MV_s} \right) \times \left(T_2^{'} + T_1^{'} \right) + C_s(0) \qquad \text{Equation 1.1.84}$$

Symbol	Parameters	Dimensions	Units	Status
$\bar{C}_s(d_{\exp})$	Average pollutant concentration in the soil during exposure period d_{exp}	M.M^{-1}	mg.kg^{-1}	C or E
D_s	Inflow to the soil by the contamination source or sources studied (local sources on and around the site)	M.M^{-1}.T^{-1}	mg.kg^{-1}.s^{-1}	C or E
$T_1^{'}$	Beginning of the exposure period$^{¥}$	T	s	E
$T_2^{'}$	End of the exposure period$^{¥}$	T	s	E
$\sum_i [FM_s]_i$	Sum of pollutant masses lost through attenuation phenomena per unit time	M.T^{-1}	mg.s^{-1}	C or E
MV_s	Bulk density of the layer considered	M.L^{-3}	kg.m^{-3}	E
S_s	Surface area of the zone considered	L^2	m^2	E
Z_s	Depth of soil layer considered	L	m	E
$C_s(0)$	Concentration in the soil at instant t=0 (instant 0 is fixed between the beginning of emissions and the beginning of exposure) (excluding background concentration)	M.M^{-1}	mg.kg^{-1}	C or E

$^{¥}$ In expressions 1.1.83 and 1.1.84, the start and end dates for exposure must be converted to seconds.

1.1.2.5.2. CASE FOR CONSTANT PARAMETERS WITH AN EXPOSURE PERIOD FINISHING AFTER THE END OF EMISSIONS

C_s must be integrated from T_1 (start of exposure period) to T_f (end of pollutant inflow to the soil from the source studied), then from T_f to T_2 (end of exposure period).

1. **If the pollutant concentration in the soil is less than the solubility limit** and if the exposure period starts at the same moment or after the beginning of pollutant inflow into the soil from the source studied,

from T_1 to T_f, we get:

$$\int_{T_1^{'}}^{T_f^{'}} C_s(t)dt = \int_{T_1^{'}}^{T_f^{'}} \left[\frac{D_s}{\sum_i k_i} \times (1 - e^{-\sum_i k_i \times t}) + C_s(0) \times e^{-\sum_i k_i \times t} \right] dt$$

Equation 1.1.85

$$\text{or } \int_{T_1^{'}}^{T_f^{'}} C_s(t)dt = \frac{D_s}{\sum_i k_i} \times (T_f^{'} - T_1^{'}) + \left(\frac{D_s}{\left(\sum_i k_i\right)^2} - \frac{C_s(0)}{\left(\sum_i k_i\right)} \right) \times \left(e^{-T_f^{'} \times \sum_i k_i} - e^{-T_1^{'} \times \sum_i k_i} \right)$$

Equation 1.1.86

and from T_f to T_2, we get:

$$\int_{T_f^{'}}^{T_2^{'}} C_s(t)dt = \int_{T_f^{'}}^{T_2^{'}} \left[C(T_f^{'}) \times e^{-\sum_i k_i \times (t - T_f^{'})} \right] dt$$

Equation 1.1.87

$$\text{or } \int_{T_f^{'}}^{T_2^{'}} C_s(t)dt = \frac{C_s(T_f^{'})}{\sum_i k_i} \times (1 - e^{-\sum_i k_i \times (T_2^{'} - T_f^{'})})$$

Equation 1.1.88

$$\text{where } C_s(T_f^{'}) = \frac{D_s}{\sum_i k_i} \times (1 - e^{-\sum_i k_i \times T_f^{'}}) + C_s(0) \times e^{-\sum_i k_i \times T_f^{'}}$$

Equation 1.1.89

hence the average concentration from T_1 to T_2:

$$\bar{C_s}(d_{\exp}) = \frac{1}{T_2^{'} - T_1^{'}} \cdot \left[\frac{D_s}{\sum_i k_i} \cdot (T_f^{'} - T_1^{'}) + \frac{D_s}{\left(\sum_i k_i\right)^2} \cdot (1 - e^{-\sum_i k_i \times (T_2^{'} - T_f^{'})}) + \left(\frac{D_s}{\left(\sum_i k_i\right)^2} - \frac{C_s(0)}{\left(\sum_i k_i\right)} \right) \cdot \left(e^{-T_2^{'} \times \sum_i k_i} - e^{-T_1^{'} \times \sum_i k_i} \right) \right]$$

Equation 1.1.90

If k=0,

from T_1 to T_f, $C_s(t) = D_s \times t + C_s(0)$

Equation 1.1.91

from T_f to T_2, $C_s(t) = C_s(T_f) = D_s \times T_f^{'} + C_s(0)$

Equation 1.1.92

and

$$\bar{C_s}(d_{\exp}) = \frac{1}{T_2^{'} - T_1^{'}} \times \left[\frac{D_s}{2} \times \left(T_f^{'2} - T_1^{'2} \right) + D_s \times T_f^{'} \times (T_2^{'} - T_f^{'}) \right] + C_s(0)$$

Equation 1.1.93

Symbol	Parameters	Dimensions	Units	Status
$\overline{C}_s(d_{exp})$	Average pollutant concentration in the soil during exposure period d_{exp}	M.M^{-1}	mg.kg^{-1}	C or E
D_s	Inflow to the soil by the contamination source or sources studied (local sources on and around the site)	M.M^{-1}.T^{-1}	mg.kg^{-1}.s^{-1}	C or E
k_i	Loss coefficient by attenuation phenomenon i	T^{-1}	s^{-1}	C or E
T_1'	Beginning of the exposure period¥	T	s	E
T_f'	End of pollutant inflow period by the contamination source(s) studied¥	T	s	E
T_2'	End of the exposure period¥	T	s	E
$C_s(0)$	Concentration in the soil at instant t=0 (instant 0 is between the beginning of emissions and the beginning of exposure) (excluding background concentration)	M.M^{-1}	mg.kg^{-1}	E

¥: In expressions from 1.1.85 to 1.1.93, the start and end dates for exposure, and the end date of pollutant inflow to the soil must be converted to seconds.

2. **If the pollutant concentration in the soil remains greater than the solubility limit throughout the exposure period** and if the exposure period starts at the same moment or after the beginning of pollutant inflow into the soil from the source studied,

from T_1 to T_f,

$$\int_{T_1}^{T_f} C_s(t)dt = \frac{1}{2} \times \left(D_s - \frac{\sum_i [FM_s]_i}{S_s \times Z_s \times MV_s} \right) \times \left(T_f'^2 - T_1'^2 \right) + C_s(0) \times \left(T_f' - T_1' \right)$$

Equation 1.1.94

from T_f to T_2, $\int_{T_f}^{T_2} C_s(t)dt = \left(C_s(T_f') - \frac{\sum_i [FM_s]_i}{S_s \times Z_s \times MV_s} \right) \times (T_2' - T_f')$

Equation 1.1.95

$$\overline{C}_s(d_{exp}) = C_s(0) + \left(D_s - \frac{\sum_i [FM_s]_i}{S_s \times Z_s \times MV_s} \right) \times \frac{\left(T_f'^2 - T_1'^2 \right)}{2 \times \left(T_2' - T_1' \right)} +$$

hence $\left(D_s - \frac{\sum_i [FM_s]_i}{S_s \times Z_s \times MV_s} \right) \times \frac{T_f' \times (T_2' - T_f')}{T_2' - T_1'} - \frac{\sum_i [FM_s]_i}{S_s \times Z_s \times MV_s} \times \frac{(T_2' - T_f')}{(T_2' - T_1')}$

Equation 1.1.96

Ref: DRC-14-141968-04378A

Symbol	Parameters	Dimensions	Units	Status
$\bar{C}_s(d_{exp})$	Average pollutant concentration in the soil during exposure period d_{exp}	M.M^{-1}	mg.kg^{-1}	C or E
D_s	Inflow to the soil by the contamination source or sources studied (local sources on and around the site)	M.M^{-1}.T^{-1}	mg.kg^{-1}.s^{-1}	C or E
T_1'	Beginning of the exposure period¥	T	s	E
T_f'	End of pollutant inflow period by the contamination source(s) studied¥	T	s	E
T_2'	End of the exposure period¥	T	s	E
$\sum_i [FM_s]_i$	Sum of pollutant masses lost through attenuation phenomena per unit time	M.T^{-1}	mg.s^{-1}	C or E
MV_s	Bulk density of the soil layer	M.L^{-3}	kg.m^{-3}	E
S_s	Surface area of the zone considered	L²	m^2	E
Z_s	Depth of soil layer	L	m	E
$C_s(0)$	Concentration in the soil at instant t=0 (instant 0 is between the beginning of emissions and the beginning of exposure) (excluding background concentration)	M.M^{-1}	mg.kg^{-1}	E

¥: In expressions from 1.1.94 to 1.1.96, the start and end dates for exposure, and the end date of pollutant inflow to the soil must be converted to seconds.

1.2. 'OUTDOOR AIR' MEDIUM

The pollutant concentration in the air equals the sum of pollutant concentrations in the air in gaseous and particulate forms.

This section focuses on:

- estimating the pollutant emission flow into the air in particulate form at the soil surface,
- estimating the pollutant emission flow into the air in gaseous form at the soil surface,
- calculating the pollutant concentration in the air from these emissive fluxes.

1.2.1. EMISSION OF POLLUTANTS IN PARTICULATE FORM AT THE SOIL SURFACE

Soil particles can be put into suspension in the air through the action of the wind or by mechanical phenomena such as road traffic or agricultural work. Emission of these particles into the air from the soil can cause persistent contamination of the air, although any industrial emission has ceased, or contaminate crops or recontaminate previously decontaminated soil from a soil source located at some distance.

Numerous factors can influence the suspension of contaminated particles from the soil. The value of the resuspended particle flux depends on:

- soil characteristics: existence of plant cover, particle size distribution, chemical properties, soil moisture;
- weather conditions: wind speed, precipitation.

For pollution from a surface deposit, we also know that the resuspended particle flux is correlated with time (this flux reduces over time).

The pollutant concentration in the outdoor air associated with resuspension of particles from the soil is used to calculate the contamination of plants by deposition of particles from the soil (cf. section 1.6.4.2) and to calculate exposure by inhalation of pollutant in particulate form (cf. section 2.1).

This concentration is estimated from the concentration of particles in suspension in the air from the soil (P_{ss}):

$$C_{ap,e\_sol} = P_{ss} \times C_s$$

Equation 1.2.1

Symbol	Parameters	Dimensions	Units	Status
C_{ap,e_sol}	Pollutant concentration in the outdoor air in particulate form, from the soil	$M.L^{-3}$	$mg.m^{-3}$	C or E
C_s	Pollutant concentration in the soil	$M.M^{-1}$	$mg.kg^{-1}$	C or E
P_{ss}	Concentration of suspended particles in the outdoor air from the soil	$M.L^{-3}$	$kg.m^{-3}$	C or E

P_{ss} is determined from empirical data. Despite the numerous measurements made, this parameter remains very uncertain, bearing in mind the great many factors that can affect its value. For practical purposes, it is often estimated from the total content of suspended particles in the air, perhaps multiplied by a coefficient representing the soil fraction in these suspended particles.

For pollution by surface deposition, contamination of the outdoor air by resuspending particles deposited on the soil is sometimes expressed using the resuspension coefficient (K). Hence:

$$C_{ap,e\_sol} = K \times C'_s$$

<div align="right">Equation 1.2.2</div>

Symbol	Parameters	Dimensions	Units	Status
C_{ap,e_sol}	Pollutant concentration in the outdoor air in particulate form, from the soil	$M.L^{-3}$	$mg.m^{-3}$	C or E
C'_s	Pollutant concentration in the soil, expressed per unit surface area	$M.L^{-2}$	$mg.m^{-2}$	C or E
K	Resuspension coefficient	L^{-1}	m^{-1}	C or E

P_{ss} and K are linked by the following relationship:

$$K = \frac{P_{ss}}{MV_s \times Z_s}$$

<div align="right">Equation 1.2.3</div>

Symbol	Parameters	Dimensions	Units	Status
K	Resuspension coefficient	L^{-1}	m^{-1}	C or E
P_{ss}	Concentration of suspended particles in the outdoor air from the soil	$M.L^{-3}$	$kg.m^{-3}$	C or E
MV_s	Bulk density of the soil layer considered	$M.L^{-3}$	$kg.m^{-3}$	E
Z_s	Depth of soil layer	L	m	E

To estimate the risk associated with exposure by inhaling particulate pollutant, the pollutant concentration adsorbed onto inhalable particles is calculated by multiplying the concentration of particulate pollutant in the air by the fraction of particles having a diameter less than 10 µm.

For particles from the soil

$$C_{ap,e\_sol\_inh} = C_{ap,e\_sol} \times f_{p\_inh}$$

<div align="right">Equation 1.2.4</div>

Symbol	Parameters	Dimensions	Units	Status
C_{ap,e_sol_inh}	Concentration of inhalable particulate pollutant (PM10) in the outdoor air and from the soil	$M.L^{-3}$	$mg.m^{-3}$	C or E
C_{ap,e_sol}	Pollutant concentration in the outdoor air in particulate form, from the soil	$M.L^{-3}$	$mg.m^{-3}$	C or E
f_{p_inh}	Fraction of suspended particles in the air, from the soil and inhalable	-	-	E

C_{ap,e_sol_inh} can also be estimated using the Cowherd model (1985), which gives the average flux over the year of inhalable particles due to wind erosion (J_{part_10pm}). Atmospheric dispersion must then be calculated from this flux and the pollutant concentration associated with the particles to obtain C_{ap,e_sol_inh} (cf. section 1.2.3).

This model is based on field measurements by Gillette (1981) and is used by the US EPA (1991, 1996a). The model considers the soil as an 'unlimited reservoir' (soil not containing a large quantity of unerodable constituents). The

expression given by Cowherd et al. provides the average annual flux of particles with diameter less than or equal to 10 µm put into suspension in the outdoor air. **It is not suitable for calculating a particle flux resulting from a one-off meteorological event**.

Except for changing units, the expression by Cowherd et al. is as follows:

$$J_{p,e\_10pm} = 10^{-8} \times (1 - f_v) \times \left(\frac{u_z}{u_z^*} \right)^3 \times F(x)$$

Equation 1.2.5

Symbol	Parameters	Dimensions	Units	Status
J_{p,e_10pm}	Average annual flux of inhalable particles put into suspension by the wind	$M.L^{-2}.T^{-1}$	kg. m^{-2}.s^{-1}	C or E
u_z	Average annual wind speed at height z on the site	$L.T^{-1}$	m.s^{-1}	E
u_z^*	Wind speed equivalent to the threshold friction velocity at the measurement height for u_z	$L.T^{-1}$	m.s^{-1}	C or E
F(x)	Function integrated in x ($x = 0,886 \times \frac{u_z^*}{u_z}$)	-	-	E
f_v	Fraction of soil with plant cover	-	-	E

The two US EPA documents refer to the equation by Cowherd et al. and propose default values to define the parameters for this equation. But using this equation on a specific site requires making use of graphic data from the original report.

Page 36 of Cowherd et al.'s (1985) report provides a graphic representation of the function F(x). Based on the value of x, Droppo et al. (1996) also suggested analytical expressions to approximate this graphical representation.

Expression 1.2.5 also involves the threshold friction velocity, which can be estimated from the modal diameter of soil aggregates (cf. figure 3.4 in the Cowherd et al. report).

In the above equation, the threshold friction velocity to be used is a corrected friction velocity, taking the presence of unerodable elements into account (stones with diameter larger than 1 cm) at the soil surface. The procedure to be followed to define this correction factor is described in the Cowherd et al. report (cf. page 22 and figure 3.5).

To obtain u_z^*, we must now calculate the wind speed at height z, which is this corrected threshold friction velocity, z being the measurement height for wind speed on the site (generally measured at 10 metres). The wind speed at height z, equivalent to the threshold friction velocity, can be calculated using the following formula:

$$u_z^* = u^* \times \frac{1}{0,4} \times \ln\left(\frac{z}{z_r} \right)$$

Equation 1.2.6

Symbol	Parameters	Dimensions	Units	Status
$u_z{}^*$	Wind speed equivalent to the threshold friction velocity at the measurement height for u_z	$L.T^{-1}$	$m.s^{-1}$	C or E
u^*	Corrected threshold friction velocity	$L.T^{-1}$	$m.s^{-1}$	E
z	Measurement height of wind speed	L	m	E
z_r	Soil roughness	L	m	E

1.2.2. EMISSION OF GASEOUS POLLUTANTS AT THE SOIL SURFACE

Emission of pollutants into the air in gaseous form is estimated for volatile and semi-volatile pollutants. The approaches described below relate to a pollutant source present in the soil or groundwater at the beginning of the study period. They are not suitable for estimating the secondary pollutant flux volatilising from a soil deposit being formed from an operational facility. The concentration in the air associated with volatilisation of an atmospheric deposition produced by an operational facility is therefore considered negligible compared to the concentration in the air from the direct flux emitted by this source. After the facility stops operating, the pollutant deposited and present in the soil can be considered as a soil source, and it is then possible to calculate the pollutant flux emitted into the air from the pollutant concentration in the soil.

1.2.2.1. CONTAMINATED SOIL

The flux emitted at the soil surface is estimated from the diffusion flux into the soil air and into soil water (J_{dif_sol}) and from the flux passing through the air boundary layer located at the soil surface (J_a).

As before, **the multiphase equilibrium between soil air, soil water and soil particles is assumed to have been reached**.

The proposed model does not take account of:

- **attenuation of the source over time (chemical or biological transformations, leaching, volatilisation, etc.): the source is considered to be in a stationary state, corresponding to an infinite source and implying steady state conditions;**
- **degradation of pollutants during transfers from the source;**
- **convective flux in the soil.**

1.2.2.1.1. CALCULATION OF DIFFUSION FLUX AT THE SOIL SURFACE

Diffusion flux in the vadose zone of the soil

The diffusion flux in the vadose zone of the soil is given locally by Fick's law:

$$J_{es} = D_{es} \times \frac{dC_{es}}{dz}$$
Equation 1.2.7

$$J_{as} = D_{as} \times \frac{dC_{as}}{dz}$$
Equation 1.2.8

where J_{es}: diffusion flux in the soil water,

J_{as}: diffusion flux in the soil air,

C_{es}: pollutant concentration in the soil water,

C_{as}: pollutant concentration in the soil air,

D_{es}: diffusion coefficient in the soil water,

D_{as}: diffusion coefficient in the soil air.

From equation 1.1.7, $C_{as} = H' \times C_{es}$
Equation 1.2.9

For soil layer i we can therefore state:

$$J_{dif\_sol,i} = J_{es,i} + J_{as,i} = DU_{a,i} \times \frac{dC_{as,i}}{dz}$$
Equation 1.2.10

where $J_{dif\_sol,i}$: diffusion flux in layer i of the vadose soil zone,

$C_{as,i}$: pollutant concentration in the soil air,

$DU_{a,i}$: multiphase diffusion coefficient of soil layer i (expressed from the concentration in soil air),

$$DU_{a,i} = \frac{D_{es,i}}{H'} + D_{as,i}$$
Equation 1.2.11

Symbol	Parameters	Dimensions	Units	Status
$DU_{a,i}$	Multiphase diffusion coefficient in soil layer i (expressed from the concentration in soil air)	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
$D_{es,i}$	Diffusion coefficient in the soil water of layer i	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
$D_{as,i}$	Diffusion coefficient in the soil air of layer i	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
H'	Henry constant (dimensionless: $H' = \dfrac{H}{R \times T_s}$)	-	-	C or E

Assuming steady state conditions and the principle of conservation of mass implies that the diffusion flux is constant with depth,

hence $\dfrac{dJ_{dif\_sol}}{dz} = 0$
Equation 1.2.12

and $\quad C_{as,i}(z) = C \times z + C'$
Equation 1.2.13

where $C_{as,i}(z)$: concentration in the soil air of layer i, at depth z (measured from the top of layer i),

C and C', two constants determined by conditions at the following limits:

$C' = C_{as,i}(0)$
Equation 1.2.14

and
$$C = \frac{C_{as,i}(l_i) - C_{as,i}(0)}{l_i}$$
<div align="right">Equation 1.2.15</div>

where l_i: thickness of layer i.

From equations 1.2.10, 1.2.13 and 1.2 15, it can be stated:

$$J_{dif\_sol,i} = DU_{a,i} \times \frac{C_{as,i}(l_i) - C_{as,i}(0)}{l_i}$$
<div align="right">Equation 1.2.16</div>

For a soil made up of n successive homogenous layers, the concentration in the air at the top of layer i equals the concentration in the air at the bottom of layer i+1 (cf. Figure 4).
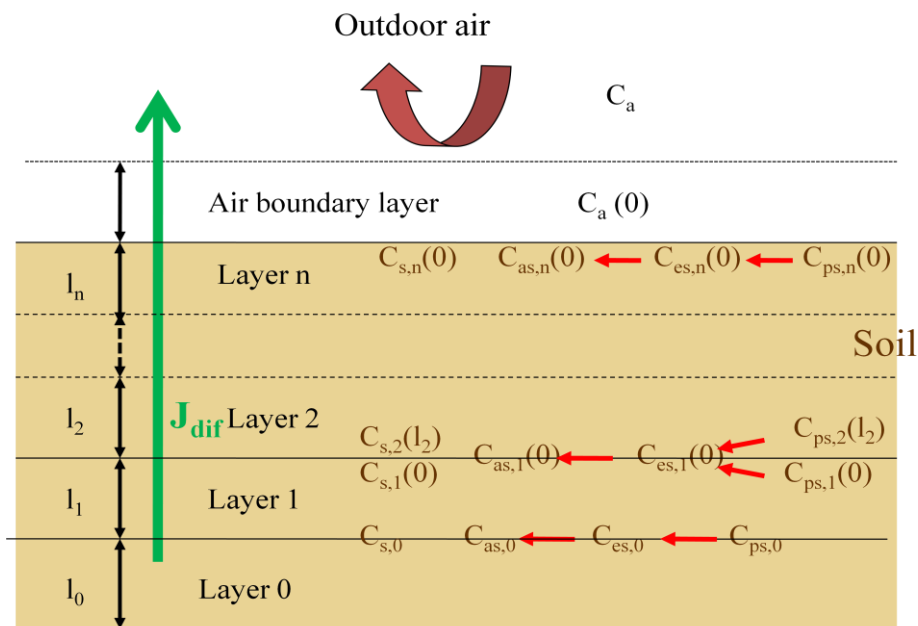
Figure 4: Schematic diagram of vapour emission model from soil to the atmosphere

The diffusion flux through each soil layer is the same, leading to:

$$\frac{DU_{a,i+1}}{l_{i+1}} \times (C_{as,i}(0) - C_{as,i+1}(0)) = \frac{DU_{a,i}}{l_i} \times (C_{as,i}(l_i) - C_{as,i}(0))$$
<div align="right">Equation 1.2.17</div>

hence
$$C_{as,i}(0) = \frac{\dfrac{DU_{a,i+1}}{l_{i+1}} \times C_{as,i+1}(0) + \dfrac{DU_{a,i}}{l_i} \times C_{as,i}(l_i)}{\dfrac{DU_{a,i+1}}{l_{i+1}} + \dfrac{DU_{a,i}}{l_i}}$$
<div align="right">Equation 1.2.18</div>

and
$$J_{dif\_sol} = \frac{1}{\dfrac{l_{i+1}}{DU_{a,i+1}} + \dfrac{l_i}{DU_{a,i}}} \times \left(C_{as,l_i}(l_i) - C_{as,i+1}(0)\right)$$
<div align="right">Equation 1.2.19</div>

So it is possible, step by step, to express the diffusion flux as a function of depth (L) of the source in the vadose zone. Hence:

$$J_{dif\_sol} = DU_{a,eq} \times \frac{C_{as,0} - C_{as,n}}{L}$$
<div align="right">Equation 1.2.20</div>

where $C_{as.0}$: pollutant concentration in the soil air at depth L,

$C_{as,n} = C_{as,n}(0)$: pollutant concentration in the soil air at the soil surface, i.e. at the top of layer n,

$DU_{a,eq}$: average multiphase diffusion coefficient (expressed from the concentration in soil air),

$$\frac{DU_{a,eq}}{L} = \frac{1}{\sum_{i=1}^{n} \frac{l_i}{DU_{a,i}}}$$

Equation 1.2.21

$l_i/Du_{a,i}$ represents the resistance of layer l_i to diffusion. For n superimposed layers, the total resistance of all layers equals the sum of the n resistances.

<u>Diffusion flux in the air boundary layer</u>

In parallel, the diffusion flux in the air boundary layer is written:

$$J_a = \frac{D_a}{d_a} \times \left(C'_{ag} - C_{ag,e} \right)$$

Equation 1.2.22

where $C_{ag,e}$: gaseous pollutant concentration in the outdoor air,

C'_{ag}: gaseous pollutant concentration in the air boundary layer,

D_a: diffusion coefficient of the pollutant in air,

d_a: height of the air boundary layer.

<u>Diffusion flux at the soil surface</u>

Assuming steady state conditions and the principle of conservation of mass leads to equality of the diffusion flux in the soil and the diffusion flux in the air boundary layer.

At equilibrium, $C'_{ag} = C_{as,n}$

and equality of J_a and J_{dif_sol} leads to stating:

$$C_{as,n} = \frac{\frac{DU_{a,eq}}{L} \times C_{as,0} + \frac{D_a}{d_a} \times C_{ag,e}}{\frac{DU_{a,eq}}{L} + \frac{D_a}{d_a}}$$

Equation 1.2.23

hence $\quad J_{dif} = \dfrac{1}{\dfrac{d_a}{D_a} + \dfrac{L}{DU_{a,eq}}} \times \left(C_{as,0} - C_{ag,e} \right)$

Equation 1.2.24

<u>Comment</u>: J_{dif} represents the net diffusion flow between the soil and the atmosphere (transfer flow by diffusion from the soil to the air and transfer flow by diffusion from the atmosphere to the air).

If the gaseous pollutant concentration in the outdoor air is low compared to that in the soil air at depth L, the worst-case assumption is that $C_{ag,e} = 0$ and we can state:

$$J_{dif} = \frac{C_{as,0}}{\frac{d_a}{D_a} + \frac{L}{DU_{a,eq}}}$$

Equation 1.2.25

Ref: DRC-14-141968-04378A

Symbol	Parameters	Dimensions	Units	Status
J_{dif}	Gaseous pollutant flux at the soil surface (soil source)	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
$C_{as,0}$	Pollutant concentration in the soil air at depth L	$M.L^{-3}$	$mg.m^{-3}$	C or E
$C_{ag,e}$	Gaseous pollutant concentration in the outdoor air	$M.L^{-3}$	$mg.m^{-3}$	C or E
$DU_{a,eq}$	Average multiphase diffusion coefficient over the transfer zone of length L (expressed from the concentration in soil air): cf. equation 1.2.21	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
D_a	Diffusion coefficient of the pollutant in air	$L^2.T^{-1}$	$m^2.s^{-1}$	E
L	Length of the diffusion zone between the point at concentration $C_{as,0}$ and the soil surface	L	m	E
d_a	Height of the air boundary layer	L	m	E

1.2.2.1.2. LIMITS ASSOCIATED WITH THIS APPROACH AND ALTERNATIVE MODELS

1.2.2.1.2.1. TAKING ACCOUNT OF CAPILLARY RISE REACHING THE SURFACE

The approach developed above does not take account of the evaporation flux associated with any capillary rise as far as the surface. This is a convective flux corresponding to evaporation of the pollutant transported by water, at the soil surface. We can state:

$$J_{conv\_sol} = E_v \times C_{es}$$

Equation 1.2.26

and if multiphase equilibrium is reached:

$$J_{conv\_sol} = E_v \times \frac{C_{as}}{H'}$$

Equation 1.2.27

where J_{conv_sol}: evaporation flux in the soil,

E_v: evaporated water flow,

C_{es}: pollutant concentration in the soil water,

C_{as}: pollutant concentration in the soil air,

H': Henry constant (dimensionless).

The calculation of total flux resulting from a convective flux and a diffusion flux is developed in section 1.3.1.1, focused on indoor air. The expression for total emission flux in the vadose soil zone (J_{tot}) is written in the same way (cf. section 1.3.1.1.3), replacing the convective flux of soil air (F_{is}) by the convective flux of evaporation, converted to air-flux-equivalent (E_v/H').

The pollutant flux is then given by the following equation:

$$J_{tot} = \frac{E_v}{H'} \times \frac{C_{as,0} - e^{-\frac{E_v}{H'}\frac{L}{DU_{a,eq}}} C_{as,n}}{1 - e^{-\frac{E_v}{H'}\frac{L}{DU_{a,eq}}}}$$

Equation 1.2.28

Assuming steady state conditions and the principle of conservation of mass leads to equality of the flux passing through the soil (J_{tot}) and the flux passing through the air boundary layer at the soil surface (J_a). From equations 1.2.22 and 1.2.28, we deduce an expression for $C_{as,n}$:

$$C_{as,n} = \cfrac{\cfrac{E_v}{H' \times \left(1 - e^{-\frac{E_v}{H'}\frac{L}{DU_{a,eq}}}\right)} \times C_{as,0} + \cfrac{D_a}{d_a} \times C_{ag,e}}{\cfrac{D_a}{d_a} + \cfrac{E_v}{H'} \times \cfrac{e^{-\frac{E_v}{H'}\frac{L}{DU_{a,eq}}}}{1 - e^{-\frac{E_v}{H'}\frac{L}{DU_{a,eq}}}}}$$

Equation 1.2.29

and

$$J_{tot} = \frac{E_v}{H'} \times \cfrac{\cfrac{D_a}{d_a} \times \left(C_{as,0} - C_{ag,e} \times e^{-\frac{E_v}{H'}\frac{L}{DU_{a,eq}}} \right)}{\left(1 - e^{-\frac{E_v}{H'}\frac{L}{DU_{a,eq}}}\right) \times \left(\cfrac{D_a}{d_a} + \cfrac{E_v}{H'} \times \cfrac{e^{-\frac{E_v}{H'}\frac{L}{DU_{a,eq}}}}{1 - e^{-\frac{E_v}{H'}\frac{L}{DU_{a,eq}}}} \right)}$$

Equation 1.2.30

If the gaseous pollutant concentration in the outdoor air is low compared to that in the soil air at depth L, the worst-case assumption is that $C_{ag,e} = 0$ and we can state:

$$J_{tot} = \cfrac{\cfrac{E_v}{H'} \times \cfrac{D_a}{d_a}}{\left(1 - e^{-\frac{E_v}{H'}\frac{L}{DU_{a,eq}}}\right) \times \left(\cfrac{D_a}{d_a} + \cfrac{E_v}{H'} \times \cfrac{e^{-\frac{E_v}{H'}\frac{L}{DU_{a,eq}}}}{1 - e^{-\frac{E_v}{H'}\frac{L}{DU_{a,eq}}}} \right)} \times C_{as,0}$$

Equation 1.2.31

Symbol	Parameters	Dimensions	Units	Status
J_{tot}	Gaseous pollutant flux at the soil surface (soil source)	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
$C_{as,0}$	Pollutant concentration in the soil air at depth L	$M.L^{-3}$	$mg.m^{-3}$	C or E
$C_{ag,e}$	Gaseous pollutant concentration in the outdoor air	$M.L^{-3}$	$mg.m^{-3}$	C or E
$DU_{a,eq}$	Average multiphase diffusion coefficient over the transfer zone considered, length L (expressed from the concentration in soil air): cf. equation 1.2.21	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
D_a	Diffusion coefficient of the pollutant in air	$L^2.T^{-1}$	$m^2.s^{-1}$	E
L	Length of the diffusion zone between the point at concentration $C_{as,0}$ and the soil surface	L	m	E
d_a	Height of the air boundary layer	L	m	E
E_v	Evaporated water flow	$L.T^{-1}$	$m.s^{-1}$	E
H'	Henry constant (dimensionless: $H' = \dfrac{H}{R \times T_s}$)	-	-	C or E

1.2.2.1.2.2. MAXIMUM POLLUTANT QUANTITY EMITTED INTO THE AIR FROM THE SOIL

The assumption of an infinite pollutant source chosen to calculate emission flux from the soil may prove to greatly overestimate. The fact of not considering attenuation of the pollution by volatilisation over time can lead to overestimating the average flux emitted over a given exposure period, all the greater when the pollution source is not so deep.

As a minimum, it is therefore necessary to check that the quantity of pollutant emitted during the period considered is less than the pollutant quantity initially present in the soil, thus:

$$\int_{T_1'}^{T_2'}(J_{dif} \times S_s)dt \leq MV_s \times C_s(T_1') \times V_{source\_sol}(T_1')$$

Equation 1.2.32

or $\quad \int_{T_1'}^{T_2'}(J_{tot}dt \times S_s) \leq MV_s \times C_s(T_1') \times V_{source\_sol}(T_1')$

Equation 1.2.33

Symbol	Parameters	Dimensions	Units	Status
J_{dif} or J_{tot}	Gaseous pollutant flux at the soil surface (soil source)	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
$V_{source\_sol}(T_1')$	Volume of the source at time T_1'	L^3	m^3	C or E
MV_s	Bulk density of the soil layer considered	$M.L^{-3}$	$kg.m^{-3}$	E
S_s	Surface of emission	L^2	m^2	E
$C_s(T_1')$	Pollutant concentration in the source at time T_1'	$M.M^{-1}$	$mg.kg^{-1}$	C or E
T_1'	Beginning of the period considered	T	s	E
T_2'	End of the period considered	T	s	E

1.2.2.1.2.3. APPROACH FOR A POLLUTANT SOURCE LEVEL WITH THE SOIL SURFACE

Where **a pollutant source is level with the soil surface** and if the concentration in air estimated from the approaches developed above prove to be a sensitive component of the study, other modelling approaches should be used. In particular we could refer to solutions presented in the US EPA document (1996a) and arising from work by Jury et al. (1984, 1990).

If **convection and degradation phenomena in the soil are not considered**, the equation for conservation of mass in the soil (or Fick's second equation) is written:

$$\frac{\partial C_s}{\partial t} = DU_a \times \frac{\partial^2 C_s}{\partial z^2}$$

Equation 1.2.34

where z: distance from the soil surface,

DU$_a$: multiphase diffusion coefficient in the soil layer studied (expressed from the concentration in soil air),

where $DU_a = \dfrac{D_{es}}{H'} + D_{as}$

Equation 1.2.35

At the following initial conditions: $C_s = C_s(0)$ for t>0 and z = + ∞ (infinite depth),

$$C_s = 0 \text{ for t>0 and z=0}$$

equation 1.2.34 gives (Jury et al., 1984):

$$J_{dif}(t) = MV_s \times C_s \times \sqrt{\frac{DU_a}{\pi \times \left(\dfrac{K_d \times MV_s}{H'} + \dfrac{\theta}{H'} + \alpha \right) \times t}}$$

Equation 1.2.36

This solution is based on the following assumptions:

- **an isotropic soil column,**
- **a uniform pollutant concentration in the soil at the initial instant,**
- **a pollutant concentration in the soil corresponding to a concentration in the soil water less than the solubility limit,**
- **compliance with the multiphase equilibrium,**
- **absence of convection and degradation phenomenon,**
- **absence of the stagnant layer of air at the soil surface,**
- **zero pollutant concentration in the air.**

For a period from T_2' to T_1', the average emission flow then equals:

$$\bar{J}_{dif\_moy}(d) = \frac{1}{T_2' - T_1'} \int_{T_1'}^{T_2'} J_{dif}(t)dt = 2 \times MV_s \times C_s \times \sqrt{\frac{DU_a}{\pi \times \left(\dfrac{K_d \times MV_s}{H'} + \dfrac{\theta}{H'} + \alpha \right)}} \times (\frac{\sqrt{T_2'} - \sqrt{T_1'}}{T_2' - T_1'})$$

Equation 1.2.37

Symbol	Parameters	Dimensions	Units	Status
$J_{dif}(t)$	Gaseous pollutant flux at the soil surface (soil source) at time t	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
$\overline{J}_{dif\_moy}(d)$	Average gaseous pollutant flux at the soil surface (soil source) over the period considered	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
C_s	Uniform pollutant concentration in the soil	$M.M^{-1}$	$mg.kg^{-1}$	C or E
DU_a	Multiphase diffusion coefficient of the pollutant in the soil layer (expressed from the concentration in soil air)	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
D_{es}	Diffusion coefficient in the soil water: cf. section 1.2.2.1.3	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
D_{as}	Diffusion coefficient in the soil air: cf. section 1.2.2.1.3	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
H'	Henry constant in dimensionless form ($H' = \dfrac{H}{R \times T_s}$)	-	-	C or E
K_d	Partition coefficient between soil particles and soil water	$L^3.M^{-1}$	$m^3.kg^{-1}$	C or E
θ	Volume fraction occupied by water in the soil	-	-	E
α	Volume fraction occupied by soil air	-	-	E
MV_s	Bulk density of the soil layer	$M.L^{-3}$	$kg.m^{-3}$	E
T_1'	Beginning of the period considered	T	s	E
T_2'	End of the period considered	T	s	E

Given the assumption of an infinite source, the pollutant quantity emitted over a given period calculated from equation 1.2.37 should also deal with the total pollutant quantity present in the soil.

Jury et al. (1990) also developed a solution to equation 1.2.34 for a finite source. With the same assumption as above, but with the following limit conditions: $C_s = C_s(0)$ at t=0,

$$C_s = 0 \text{ for t=0 and } z > H_0,$$
$$C_s = 0 \text{ for t>0 and } z = 0$$

equation 1.2.34 gives:

$$J_{dif}(t) = MV_s \times C_s(0) \times \sqrt{\frac{DU_a}{\pi \times \left(\dfrac{K_d \times MV_s}{H'} + \dfrac{\theta}{H'} + \alpha \right) \times t}} \times \left(1 - \exp^{ -\dfrac{H_0{}^2 \times \left(\frac{K_d \times MV_s}{H'} + \frac{\theta}{H'} + \alpha \right)}{4 \times DU_a \times t} } \right)$$

<div align="right">Equation 1.2.38</div>

Symbol	Parameters	Dimensions	Units	Status
$J_{dif}(t)$	Gaseous pollutant flux at the soil surface at time t (soil source)	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
$C_s(0)$	Uniform pollutant concentration in the soil layer, with a thickness of H_0 at t=0	$M.M^{-1}$	$mg.kg^{-1}$	C or E
DU_a	Multiphase diffusion coefficient in the soil (expressed from the concentration in soil air)	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
H'	Henry constant in dimensionless form ($H' = \dfrac{H}{R \times T_s}$)	-	-	C or E
θ	Volume fraction occupied by water in the soil	-	-	E
α	Volume fraction occupied by soil air	-	-	E
MV_s	Bulk density of the soil layer	$M.L^{-3}$	$kg.m^{-3}$	E
H_0	Thickness (= depth of bottom) of polluted layer at t=0	L	m	E

1.2.2.1.3. CALCULATING DIFFUSION COEFFICIENTS INTO THE SOIL AIR AND SOIL WATER

The diffusion coefficient in soil air is calculated from the diffusion coefficient of the pollutant in air, adjusted for the tortuosity of the medium (which takes account of detours that the pollutant has to take to reach the surface), according to the expression provided by Millington and Quirk (1961):

$$D_{as} = D_a \times \frac{\alpha^{\frac{10}{3}}}{n^2}$$

<div align="right">Equation 1.2.39</div>

In the same way, the diffusion coefficient in the soil water is calculated from the diffusion coefficient of the pollutant in water, using the following expression:

$$D_{es} = D_e \times \frac{\theta^{\frac{10}{3}}}{n^2}$$

<div align="right">Equation 1.2.40</div>

Symbol	Parameters	Dimensions	Units	Status
D_{es}	Diffusion coefficient in the soil water	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
D_{as}	Diffusion coefficient in the soil air	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
D_e	Diffusion coefficient of the pollutant in water	$L^2.T^{-1}$	$m^2.s^{-1}$	E
D_a	Diffusion coefficient of the pollutant in air	$L^2.T^{-1}$	$m^2.s^{-1}$	E
n	Soil porosity (volume fraction): n=α+θ	-	-	C or E
θ	Volume fraction occupied by water in the soil	-	-	E
α	Volume fraction occupied by soil air	-	-	E

1.2.2.2. CONTAMINATED GROUNDWATER

When the contamination source is in the groundwater, transfer across the capillary fringe can be considered.

<u>Flux in the capillary fringe</u>

Transfer across the capillary fringe involves:

- a convective flux associated with evaporation,
- a diffusion flux in the air[4] and in the water.

Locally, in the capillary fringe, evaporation flux is written as:

$$J_{conv\_cap} = E_v \times C_{es\_cap}$$

Equation 1.2.41

where $C_{es\_cap} = \dfrac{C_{as\_cap}}{H'}$

Equation 1.2.42

where $J_{conv,cap}$: evaporation flux in the capillary fringe,

  E_v: evaporated water flow,

  C_{es_cap}: pollutant concentration in the interstitial water of the capillary fringe,

  C_{as_cap}: pollutant concentration in the air of the capillary fringe,

  H': Henry constant (dimensionless).

Diffusive flux is written as for the vadose zone, replacing the multiphase diffusion coefficient for the soil by that for the capillary fringe, and the concentration in soil air by that for the air in the capillary fringe.

$$J_{dif\_cap} = DU_{eq\_cap} \times \dfrac{dC_{as\_cap}}{dz}$$

Equation 1.2.43

The calculation of total flux resulting from a convective flux and a diffusion flux is developed in section 1.3.1.1, for the vadose soil zone. The expression for total emission flow across the capillary fringe is developed in section 1.3.1.2. It is expressed as follows:

$$J_{tot\_cap} = \dfrac{E_v}{H'} \dfrac{C_{as\_nap} - e^{-\frac{E_v}{H'} \frac{L_{cap}}{DU_{eq\_cap}}} C_{as,0}}{1 - e^{-\frac{E_v}{H'} \frac{L_{cap}}{DU_{eq\_cap}}}}$$

Equation 1.2.44

where $C_{as,0}$: pollutant concentration in the soil air at the top of the capillary fringe,

  L_{cap}: thickness of the capillary fringe,

  $C_{as,nap}$: pollutant concentration in the soil air at the surface of the groundwater.

and $C_{as\_nap} = H' \times C_{e\_nap}$

Equation 1.2.45

  where C_{e_nap}: concentration is dissolved form in the groundwater

---

[4] Given the high content of soil water at the capillary fringe, all connections between bubbles of residual air and any continuous diffusion into the air may be prevented. Despite this, the choice has been made here to present a complete expression for diffusion flux. *Ultimately*, the final equation obtained can be used and parametrisation determines whether or not to select diffusion in air at the capillary fringe. It is worth noting that, given the very low diffusivity in water compared to air, taking account of diffusion in air at the capillary fringe significantly increases diffusion.

<u>Flux at the soil surface</u>

Assuming steady state conditions and the principle of conservation of mass leads to equality of the flux at the soil surface (J_{tot}) and the flux crossing the capillary fringe (J_{tot_cap}). Hence:

$$J_{tot} = \frac{E_v}{H'} \times \frac{C_{as\_nap} - e^{-\frac{Ev}{H'}\frac{L_{cap}}{DU_{eq\_cap}}} C_{as,0}}{1 - e^{-\frac{Ev}{H'}\frac{L_{cap}}{DU_{eq\_cap}}}} \qquad \text{Equation 1.2.46}$$

1. **If the pollutant considered is more volatile that water and in the absence of capillary rise as far as the soil surface,** $C_{as,0}$ is calculated from equations 1.2.24 and 1.2.44, taking L as the thickness of the unsaturated layer,

$$\text{hence } C_{as,0} = \frac{\dfrac{E_v}{H'} \times \dfrac{C_{as\_nap}}{1 - e^{-\frac{Ev}{H'}\frac{L_{cap}}{DU_{eq\_cap}}}} + \dfrac{C_{ag,e}}{\dfrac{L}{DU_{a,eq}} + \dfrac{d_a}{D_a}}}{\dfrac{E_v}{H'} \times \dfrac{e^{-\frac{Ev}{H'}\frac{L_{cap}}{DU_{eq\_cap}}}}{1 - e^{-\frac{Ev}{H'}\frac{L_{cap}}{DU_{eq\_cap}}}} + \dfrac{1}{\dfrac{L}{DU_{a,eq}} + \dfrac{d_a}{D_a}}} \qquad \text{Equation 1.2.47}$$

If the pollutant concentration in the outdoor air in gaseous form is low compared to the concentration in the air at the top of the capillary fringe, the worst-case assumption is that $C_{ag,e} = 0$ and we can state:

$$C_{as,0} = \frac{\dfrac{E_v}{H'} \times \dfrac{C_{as\_nap}}{1 - e^{-\frac{Ev}{H'}\frac{L_{cap}}{DU_{eq\_cap}}}}}{\dfrac{E_v}{H'} \times \dfrac{e^{-\frac{Ev}{H'}\frac{L_{cap}}{DU_{eq\_cap}}}}{1 - e^{-\frac{Ev}{H'}\frac{L_{cap}}{DU_{eq\_cap}}}} + \dfrac{1}{\dfrac{L}{DU_{a,eq}} + \dfrac{d_a}{D_a}}} \qquad \text{Equation 1.2.48}$$

2. **If the water table is shallow and the capillary fringe level with the soil surface**, $C_{as,0}$ is calculated from equations 1.2.22 and 1.2.44, taking $C_{as,0}$ as equal to C'_{ag} at equilibrium,

$$\text{hence } C_{as,0} = \frac{\dfrac{E_v}{H'} \times \dfrac{C_{as\_nap}}{1 - e^{-\frac{Ev}{H'}\frac{L_{cap}}{DU_{eq\_cap}}}} + \dfrac{D_a}{d_a} \times C_{ag,e}}{\dfrac{E_v}{H'} \times \dfrac{e^{-\frac{Ev}{H'}\frac{L_{cap}}{DU_{eq\_cap}}}}{1 - e^{-\frac{Ev}{H'}\frac{L_{cap}}{DU_{eq\_cap}}}} + \dfrac{D_a}{d_a}} \qquad \text{Equation 1.2.49}$$

If the gaseous pollutant concentration in the outdoor air is low compared to the concentration in the air at the top of the capillary fringe, the worst-case assumption is that $C_{ag,e} = 0$ and we can state:

$$C_{as,0} = \cfrac{\cfrac{E_v}{H^{'}} \times \cfrac{C_{as\_nap}}{1 - e^{-\frac{Ev}{H^{'}} \frac{L_{cap}}{DU_{eq\_cap}}}}}{\cfrac{E_v}{H^{'}} \times \cfrac{e^{-\frac{Ev}{H^{'}} \frac{L_{cap}}{DU_{eq\_cap}}}}{1 - e^{-\frac{Ev}{H^{'}} \frac{L_{cap}}{DU_{eq\_cap}}}} + \cfrac{D_a}{d_a}}$$

Equation 1.2.50

Symbol	Parameters	Dimensions	Units	Status
J_{tot}	Gaseous pollutant flux at the soil surface (groundwater source)	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
$C_{as,0}$	Pollutant concentration in the air at the top of the capillary fringe	$M.L^{-3}$	$mg.m^{-3}$	C or E
E_v	Evaporated water flow	$L.T^{-1}$	$m.s^{-1}$	E
$C_{ag,e}$	Gaseous pollutant concentration in the outdoor air	$M.L^{-3}$	$mg.m^{-3}$	C or E
C_{as_nap}	Pollutant concentration in the air at the surface of the groundwater	$M.L^{-3}$	$mg.m^{-3}$	C or E
C_{e_nap}	Dissolved concentration of pollutant in the groundwater	$M.L^{-3}$	$mg.m^{-3}$	C or E
$DU_{a,eq}$	Average multiphase diffusion coefficient in the vadose soil zone (expressed from the concentration in soil air): cf. equation 1.2.21	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
DU_{eq_cap}	Average multiphase diffusion coefficient in the capillary fringe (expressed from the concentration in soil air): cf. equation 1.2.21	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
D_a	Diffusion coefficient of the pollutant in air	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
L	Thickness of the vadose zone	L	m	E
L_{cap}	Thickness of the capillary fringe	L	m	E
d_a	Height of the air boundary layer	L	m	E
H'	Henry constant (dimensionless: $H^{'} = \dfrac{H}{R \times T_s}$)	-	-	C or E

Comments:

1. Estimating the concentration in water of the capillary fringe and groundwater using equations 1.2.42 and 1.2.45, respectively, corresponds to a potentially overestimating assumption where multiphase equilibrium is assumed to have been reached.

2. For a submerged pollutant source (eg. pollutant more dense than water) and a 'badly-mixed' aquifer, transfer in the saturated zone must be considered. It is estimated by considering the soil saturated zone as an additional layer (without air) to the capillary fringe and by including diffusion in the groundwater in the model.

   To do so, in equations 1.2.43 to 1.2.50,

   - the diffusion coefficient DU_{eq_cap} is replaced by a multi-layer diffusion coefficient $DU_{eq\_cap\_nap}$ including the diffusion coefficient in the

groundwater per equation 1.2.21 (resistance of all layers equals the sum of resistances for the different layers);

- the thicknesses of the capillary fringe L_{cap} is replaced by the sum of thicknesses of the capillary fringe and the soil saturated zone to be crossed, L_{cap_nap}.

Ref: DRC-14-141968-04378A

1.2.3. ATMOSPHERIC DISPERSION AND CALCULATING THE AIR CONCENTRATION FROM THE FLUX AT THE SOIL SURFACE

For atmospheric emissions of pollutants from a chimney, INERIS uses atmospheric dispersion software to calculate concentrations in the air.

For simple cases, it is possible to use models based on a Gaussian approach. First-generation Gaussian models used an atmospheric stability classification (eg. Pasquill classification), while second-generation Gaussian models are based on a parametric representation of the height of the boundary layer. This second approach is used to continuously characterise atmospheric conditions and take account of changes in the boundary layer with altitude.

Most of these models include specific parametrisation to take account of the effect of buildings and relief under simple conditions, by calculating changes in the wind field due to the land form.

The input data needed to use these models relate to:

- the description of the pollution source: location, geometry, characteristics of discharges and pollutants, emitted flux,
- sequential meteorological data,
- characteristics of the study scope likely to influence dispersion: roughness, relief, buildings.

To model more complex situations (eg. enclosed valleys), Eulerian models are used to represent the wind field and Eulerian, Lagrangian or Gaussian-puff models are used to model dispersion. For information, the reader can refer the LCSQA (2002) report.

Some Gaussian models also take account of surface and/or volume sources, possibly located on the soil. Nonetheless, depending on the required level of analysis, and given the uncertainties associated with calculating the surface emission flow, a simple mass balance can sometimes be enough to estimate the concentration in the air immediately downwind of the source. This approach is sometimes called 'box model' (cf. Figure 5). The only meteorological parameter required is therefore the wind speed and the concentration in the air is assumed homogeneous in the dispersion volume considered.
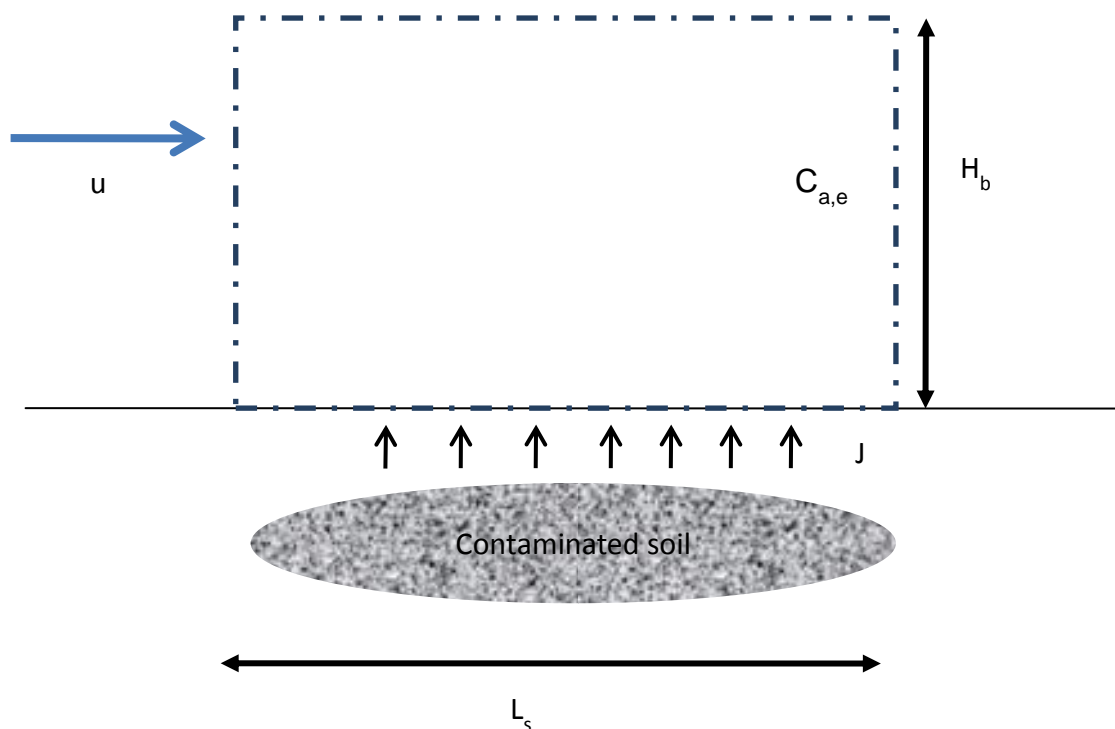
Figure 5: Schematic diagram of the 'box model'

For a source in the soil or groundwater located at the site studied, the mass balance equation leads to:

$$H_b \times L_s \times l_s \times \frac{dC_{a,e}}{dt} = J \times L_s \times l_s - C_{a,e} \times u \times H_b \times l_s$$

Equation 1.2.51

As steady state conditions are reached rapidly[5], we can state:

$$C_{a,e} = \frac{J \times L_s}{u \times H_b}$$

Equation 1.2.52

Symbol	Parameter	Dimensions	Units	Status
$C_{a,e}$	Concentration in outdoor air attributable to the soil or groundwater source immediately downwind of the site	$M.L^{-3}$	$mg.m^{-3}$	C or E
J	Flux of pollutant per unit area and time (particulate and/or gaseous flux with a soil or groundwater source located at the site)	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
H_b	Height of the 'box' (generally taken as equal to the breathing height of individuals)	L	m	E
L_s	Dimension of the source parallel to the wind direction	L	m	E
u	Wind speed in the box	$L.T^{-1}$	$m.s^{-1}$	E

(l_s: Dimension of the emission source perpendicular to the wind direction)

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[5] When $T = 3 \times L_s / u$, $C_{a,e}$ reaches 95% of its steady-state value (see the demonstration in section 1.7.1.2.3). As a result, for a contaminated site 100 metres long, with a wind speed of 3 $m.s^{-1}$, the pollutant concentration in the downwind air is close to steady state conditions after 100 seconds of emission.

<u>Comment</u>: The pollutant concentration in the air calculated using the mass balance is the concentration in outdoor air attributable to the source studied (excluding background concentration). It is calculated from the sums of particulate and gaseous fluxes, themselves calculated from concentrations in the soil, excluding background concentration. Even if the net diffusion flux depends on the difference between the total concentration in the soil air at the source and the total gaseous concentration at the soil surface, this calculation method has been selected because background concentrations are assumed low in comparison with the concentration attributable to the source in the soil air at this source.

The total pollutant concentration in outdoor air is then obtained by adding the background concentration in the outdoor air (cf. section 4) to the concentration in the outdoor air attributable to the soil source or groundwater source ($C_{a,e}$).

1.3. 'INDOOR AIR' MEDIUM

As for outdoor air, the pollutant concentration in indoor air equals the sum of pollutant concentrations in the air in gaseous and particulate forms.

INERIS has not worked on modelling the transfer of particulate pollutants from outdoor air to indoor air, nor on that for particulate pollutants fluxes from the floor indoors. The only approach used until then is identical to that presented in CSOIL (RIVM, 2007). It consists of calculating the pollutant concentration in particulate form in the indoor air by multiplying the pollutant concentration in particulate form in the outdoor air by a factor representing the fraction of particles transferred from the exterior to the interior:

$$C_{ap,i} = C_{ap,e} \times f_{ext\_int}$$

Equation 1.3.1

Symbol	Parameter	Dimensions	Units	Status
$C_{ap,i}$	Particulate pollutant concentration in the indoor air	$M.L^{-3}$	$mg.m^{-3}$	C or E
$C_{ap,i}$	Particulate pollutant concentration in the outdoor air	$M.L^{-3}$	$mg.m^{-3}$	C or E
f_{ext_int}	Fraction of particles transferred from the exterior to the interior	-	-	E

The rest of this section will therefore be entirely dedicated to estimating the gaseous pollutant concentration in the indoor air.

In the case of soil polluted by volatile organic substances, vapour transfer from the soil to the indoor air, and the inhalation following from it, can constitute the main exposure pathway.

Three vapour emission models from soil to indoor air are typically used in France:

- the Johnson and Ettinger model (1991), recommended by the US EPA (2004a), which takes account of convection and diffusion of vapours in the soil and at floor level of a building;

- the VOLASOIL model (Waitz et al., 1996), currently recommended by RIVM (Dutch institute for protection of health and environment). This model, designed to represent the transfer of pollutants in the indoor air of a building constructed over a crawl space from a source in the soil or in a shallow groundwater, takes into account convection and diffusion of vapours in the soil and convection through the floor;

- the model previously-recommended by RIVM, and used in the 1994 version of CSOIL (van den Berg, 1994), in HESP (Veerkamp and ten Berge, 1994, Shell Global Solutions, 1995) or in Risc Human (Van Hall Larestein). This model considers the evaporation of contaminants and diffusion of vapours from the soil to the crawl space.

This section presents an approach based on the VOLASOIL principles, but modified and generalised in order to be able to consider several different soil layers or even a (or several) soil layer(s) on which the floor of a building is sited;

A second approach matching the Johnson and Ettinger model will be included in this document at a later date. In the meantime, readers are referred to the US EPA (2004) document.

The approach used in CSOIL is not discussed, because it is a special case of the VOLASOIL approach, in which the effect of convection is negligible.

1.3.1. APPROACH DERIVED FROM THE VOLASOIL MODEL

This approach has been detailed in two documents (Hazebrouck et al., 2005, DRC-05-57281-DESP/R01a), which forms the basis for the description below. The reader should refer to them for more information, particularly in terms of setting parameters.

This approach, derived from VOLASOIL, deals with situations where the contamination source is located in the vadose zone and those where the groundwater is contaminated.

It takes into account:

- four successive compartments: the saturated zone, the capillary fringe, the vadose zone and the indoor air;

- three transfer mechanisms: diffusion in water in the vadose zone and capillary fringe, diffusion in the air in the vadose zone and capillary fringe and convection in the air in the vadose zone and capillary fringe[6].

As in the previous sections, the model assumes the multiphase equilibrium between soil air, soil water and soil particles.
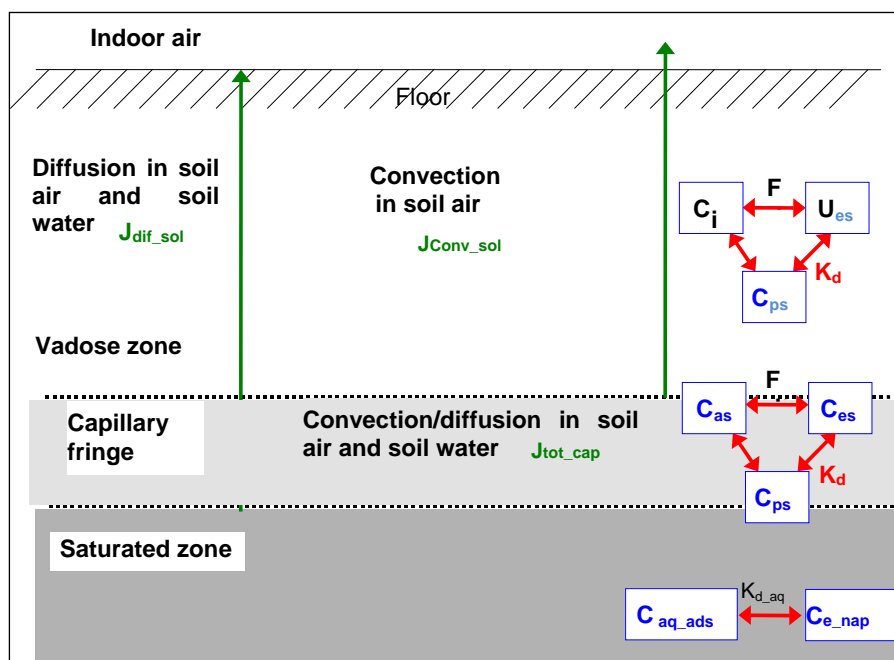
Figure 6: Schematic diagram of vapour emission model from soil to the indoor air of a building

However, the model does not take into account:

- natural attenuation of the source over time: the source is considered to be in a stationary state, corresponding to an infinite source and implying steady state conditions;

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[6] Diffusion in the soil water in the vadose zone, diffusion in the soil air of the capillary fringe and convection, associated with evaporation from the capillary fringe, are not considered in the original VOLASOIL model (Waitz et al., 1996)

- degradation of pollutants during transfers between the source and the soil surface.

1.3.1.1. TOTAL EMISSION FLUX THROUGH THE VADOSE ZONE

Depending on the type of construction, emission flux is considered, either through the vadose zone of the soil as far as the crawl space or through the vadose zone of the soil and concrete slab forming the floor of the living area.

1.3.1.1.1. EXPRESSION OF DIFFERENT FLUXES

Convective flux

A convective flux between the vadose zone and the building (crawl space or living area) is assumed to be generated by the pressure difference between these two media. This pressure difference may be due:

- to the temperature difference associated with heating,
- to mechanical ventilation inside the building,
- to a lesser degree, to the action of wind on the walls of the building.

Locally, the convective flux is written:

$$J_{conv} = F_{is} \times C_{as} \hspace{4cm} \text{Equation 1.3.2}$$

where C_{as}: pollutant concentration in the soil air,

F_{is}: flux of air from the soil to the building (living space, crawl space or basement).

Diffusion flux

As for emission to the outdoor air (cf. section 1.2.2.1.1), the local expression for diffusion flux in the vadose zone is given by Fick's law:

$$J_{dif\_sol} = D_{es} \times \frac{dC_{es}}{dz} + D_{as} \times \frac{dC_{as}}{dz} \hspace{2cm} \text{Equation 1.3.3}$$

or $\hspace{1cm} J_{dif\_sol} = DU_a \times \frac{dC_{as}}{dz} \hspace{3cm} \text{Equation 1.3.4}$

where C_{es}: pollutant concentration in the soil water,

DU_a: multiphase diffusion coefficient in the soil (expressed from the concentration in the soil air):

$$DU_a = \frac{D_{es}}{H'} + D_{as} \hspace{4cm} \text{Equation 1.3.5}$$

Symbol	Parameters	Dimensions	Units	Status
DU_a	Multiphase diffusion coefficient in the soil (expressed from the concentration in soil air)	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
D_{es}	Diffusion coefficient in the soil water (the expression for D_{es} is given in section 1.2.2.1.3)	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
D_{as}	Diffusion coefficient in the soil air (the expression for D_{as} is given in section 1.2.2.1.3)	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
H'	Henry constant (dimensionless: $H' = \dfrac{H}{R \times T_s}$)	-	-	C or E

Ref: DRC-14-141968-04378A

Total flux through the vadose zone of the soil

Locally, the total emission flux in the vadose zone (J_{tot}) therefore equals:

$$J_{tot} = F_{is} \times C_{as} + DU_a \times \frac{dC_{as}}{dz}$$

Equation 1.3.6

Comment: the evaporation flux associated with any capillary rise as far as the surface (eg. a cave with a beaten earth flow), is not considered here. It could be taken into account, as for the outdoor air, by adding a second convective flux.

This flux would equal: $J_{conv,sol} = E_v \times \dfrac{C_{as}}{H'}$ (cf. section 1.2.2.1.2.1).

1.3.1.1.2. CALCULATION OF TOTAL FLUX FOR A MONOLAYER

Let's consider the case of a homogeneous soil layer going from the contamination source as far as the soil surface. The following concepts are adopted:

- $C_{as,i}$ (z): pollutant concentration in the soil air, in layer i as a function of depth z from the top of the layer,
- l_i: thickness of layer i,
- $DU_{a,i}$: multiphase diffusion coefficient in layer i.

According to **assumptions regarding steady state conditions and conservation of mass**, flux J_{tot} is constant with depth,

hence $\dfrac{dJ_{tot}}{dz} = 0$,

Equation 1.3.7

and $\quad F_{is} \times \dfrac{dC_{as,i}}{dz} + DU_{a,i} \times \dfrac{d^2 C_{as,i}}{dz^2} = 0$

Equation 1.3.8

The solution to this differential equation is given by:

$$C_{as,i}(z) = -F_{is} \times DU_{a_i} \times C_i \times e^{-\frac{F_{is}}{DU a_i} z} + C_i{}'$$

Equation 1.3.9

where C_i and C'_i are two constants, determined by conditions at the limits of layer i.

By stating: $\chi_i = e^{-\frac{F_{is}}{DU_{a,i}} \times l_i}$, these conditions at the limits are written:

$$C_{as,i}(l_i) - C_{as,i}(0) = -F_{is} \times DU_{a,i} \times (\chi_i - 1) \times C_i$$

Equation 1.3.10

and $\quad C_{as,i}(0) = -F_{is} \times DU_{a,i} \times C_i + C_i{}'$

Equation 1.3.11

hence $C_i = \dfrac{C_{as,i}(l_i) - C_{as,i}(0)}{F_{is} \times DU_{a,i} \times (1 - \chi_i)}$

Equation 1.3.12

and $\quad C_i{}' = \dfrac{C_{as,i}(l_i) - C_{as,i}(0) \times \chi_i}{(1 - \chi_i)}$

Equation 1.3.13

In the equation for local emission flux, replacing $C_{as,i}$ by equation 1.3.9, as well as C_i and $C_{i'}$ by expressions 1.3.12 and 1.3.13, we obtain:

$$J_{tot} = F_{is} \times C_i{}' = \dfrac{F_{is}}{1 - \chi_i} \times (C_{as,i}(l_i) - C_{as,i}(0) \times \chi_i)$$

Equation 1.3.14

hence $J_{tot} = \dfrac{F_{is}}{1 - e^{-\frac{F_{is}}{DU_{a,i}} \times l_i}} \times \left(C_{as,i}(l_i) - C_{as,i}(0) \times e^{-\frac{F_{is}}{DU_{a,i}} \times l_i} \right)$

Equation 1.3.15

Symbol	Parameters	Dimensions	Units	Status
J_{tot}	Gaseous pollutant flux in the vadose zone of the soil	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
F_{is}	Air flux from the soil to the building due to convection	$L.T^{-1}$	$m.s^{-1}$	C or E
$C_{as,i}(0)$	Pollutant concentration in the soil air, at the top of layer i	$M.M^{-3}$	$mg.m^{-3}$	C or E
$C_{as,i}(l_i)$	Pollutant concentration in the soil air, at the bottom of layer i	$M.M^{-3}$	$mg.m^{-3}$	C or E
l_i	Thickness of layer i	L	m	E
$DU_{a,i}$	Multiphase diffusion coefficient in layer i of the soil (expressed from the concentration in the soil air)	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E

Comment: this formula is found in the document by Waitz et al. (page 68, formula 74 and page 13, formula 16), replacing $C_{as,i}(0)$ by the concentration in the air at the surface (C_0), $C_{as,i}(l_i)$ by the concentration in the soil air at the source (C_{sa}) and l_i by the height of the soil column between the source and the crawl space (L_s). It is then simplified, by considering that the concentration in the air at the surface is negligible relative to C_{sa}.

1.3.1.1.3. CALCULATION OF TOTAL FLUX FOR MULTIPLE LAYERS

If, this time, we consider n successive homogenous soil layers, incremented in increasing i from the contamination depth (i=0) as far as the surface (i=n for the layer in contact with the air), from equation 1.3.15 we can deduce for each layer i:

$$C_{as,i}(l_i) = \frac{J_{tot}}{F_{is}} \times (1 - \chi_i) + C_{as,i}(0) \times \chi_i$$

Equation 1.3.16

where $\chi_i = e^{-\frac{F_{is}}{DU_{a,i}} \times l_i}$

Since the concentration in the soil air is continuous, values of C_{as} at the top of layer i and bottom of layer i+1 are equal (cf. Figure 7). $C_{as,i}$ is this concentration at the interface between layers:

$$C_{as,i} = C_{as,i}(0) = C_{as,i+1}(l_{i+1})$$

Equation 1.3.17

Assumptions of steady state conditions and conservation of mass lead to a constant emission flux J_{tot} with depth. It can be stated for all i:

$$J_{tot} = J_{tot,i}$$

Equation 1.3.18
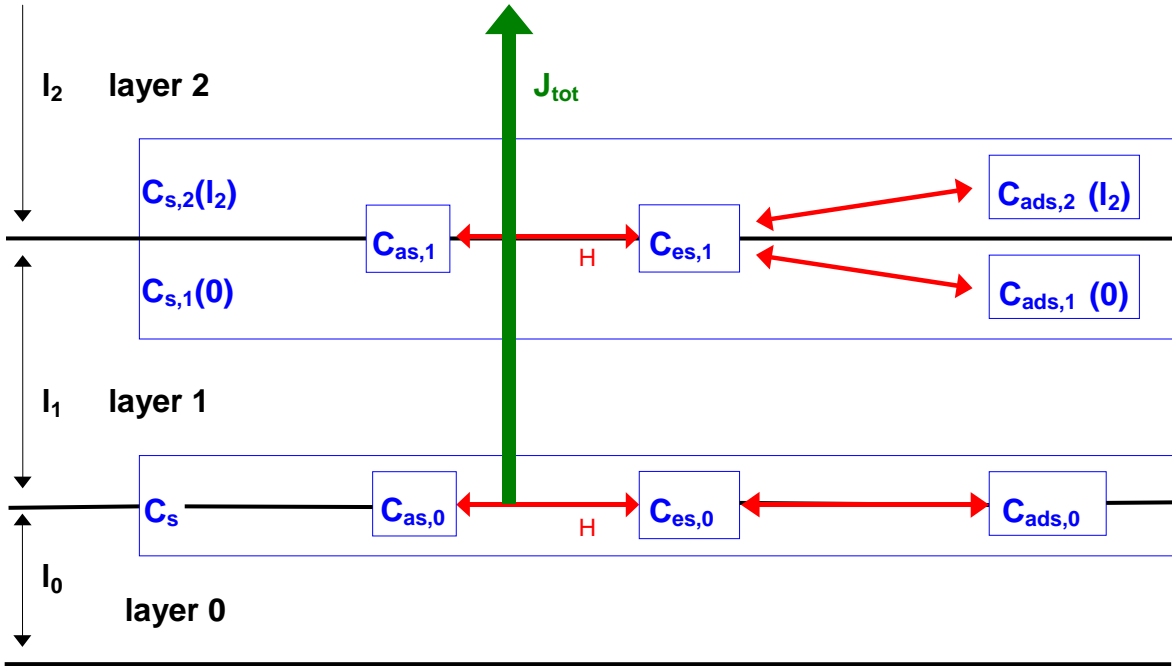
Figure 7: Modelling diffusion and convection in a multi-layer soil

For all i between 1 and n, equation 1.3.16 is therefore written:

$$C_{as,i-1} = \frac{J_{tot}}{F_{is}} \times (1 - \chi_i) + C_{as,i} \times \chi_i \qquad \text{Equation 1.3.19}$$

hence, by iteration over n layers, from the contamination zone ($C_{as,0} = C_{as,i=0}$) to the surface ($C_{as,surf} = C_{as,n}$):

$$C_{as,0} = \frac{J_{tot}}{F_{is}} \times \left[(1 - \chi_1) + \chi_1(1 - \chi_2) + \chi_1 \cdot \chi_2 (1 - \chi_3) + \dots + \prod_{i=1}^{n-1} \chi_i (1 - \chi_n) \right] + C_{as,n} \prod_{i=1}^{n} \chi_i$$

Equation 1.3.20

$$C_{as,0} = \frac{J_{tot}}{F_{is}} \times \left(1 - \prod_{i=1}^{n} \chi_i \right) + C_{as,n} \prod_{i=1}^{n} \chi_i \qquad \text{Equation 1.3.21}$$

$$C_{as,0} = \frac{J_{tot}}{F_{is}} \times \left(1 - e^{-F_{is} \times \sum_{i=1}^{n} \frac{l_i}{DU_{a,i}}} \right) + C_{as,n} \times e^{-F_{is} \times \sum_{i=1}^{n} \frac{l_i}{DU_{a,i}}} \qquad \text{Equation 1.3.22}$$

and
$$J_{tot} = F_{is} \times \frac{C_{as,0} - C_{as,n} \times e^{-F_{is} \times \sum_{i=1}^{n} \frac{l_i}{DU_{a,i}}}}{\left(1 - e^{-F_{is} \times \sum_{i=1}^{n} \frac{l_i}{DU_{a,i}}} \right)} \qquad \text{Equation 1.3.23}$$

If $DU_{a,eq}$ is the average multiphase diffusion coefficient for n layers (expressed ito the concentration in the air), we can write:

$$J_{tot} = F_{is} \times \frac{C_{as,0} - C_{as,n} \times e^{-F_{is} \times \frac{L}{DU_{a,eq}}}}{\left(1 - e^{-F_{is} \times \frac{L}{DU_{a,eq}}}\right)}$$

Equation 1.3.24

where $L = \sum_{i=1}^{n} l_i$, distance between the concentration point $C_{as,0}$ and the interior surface of the building (crawl space, basement or living area),

and $\quad \frac{L}{DU_{a,eq}} = \sum_{i=1}^{n} \frac{l_i}{DU_{a,i}}$

Equation 1.3.25

If the concentration in the soil air at the surface in contact with the atmosphere is low compared to the concentration in the soil air at the source, we consider that $C_{as,n} = 0$ and so obtain:

$$J_{tot} = F_{is} \times \frac{C_{as,0}}{\left(1 - e^{-F_{is} \times \frac{L}{DU_{a,eq}}}\right)}$$

Equation 1.3.26

Symbol	Parameters	Dimensions	Units	Status
J_{tot}	Gaseous pollutant flux at the surface of a building (for contaminated soil)	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
F_{is}	Air flux from the soil to the building due to convection	$L.T^{-1}$	$m.s^{-1}$	C or E
$C_{as,n}$	Pollutant concentration in the soil air at the surface (crawl space, basement or interior of the building)	$M.L^{-3}$	$mg.m^{-3}$	C or E
$C_{as,0}$	Pollutant concentration in the soil air, at the depth considered	$M.L^{-3}$	$mg.m^{-3}$	C or E
L	Length of the transfer zone in the vadose zone, from the concentration point $C_{as,0}$ to the interior of the building (crawl space, basement or living area)	L	m	E
$DU_{a,eq}$	Average multiphase diffusion coefficient over the transfer zone considered, length L (expressed in relation to the air concentration)	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E

Comments:

1. This expression is equivalent to that obtained for a monolayer, with the term for average resistance to multi-layer diffusion ($L/DU_{a,eq}$) replacing the term used for the monolayer (l_i/DU_a).

2. When the air flux F_{is} tends to 0,

$$e^{-F_{is} \times \frac{L}{DU_{a,eq}}} \approx 1 - F_{is} \times \frac{L}{DU_{a,eq}}$$

Equation 1.3.27

emission flux J_{tot} then equals the diffusion flux alone:

$J_{dif} = DU_{a,eq} \times (C_{as,0} - C_{as,n}) / L \approx DU_{eq} \times C_{as,0} / L$

Equation 1.3.28

Similarly, for poorly-diffusing substances (average diffusion coefficient $DU_{a,eq}$ tending to 0), we find the gaseous emission flux by convection alone, using J_{tot}:

$$J_{conv} = F_{is} \times C_{as,0}$$

Equation 1.3.29

3. The result for both transport modes combined is less than the sum of the two transfers taken independently.

In fact, if we state $x = F_{is} \times L/DU_{a,eq}$,

$$\frac{J_{tot} - (J_{dif} + J_{conv})}{C_{as,0}} = \frac{x\, e^{-x} - 1 + e^{-x}}{(1 - e^{-x})\,(DU_{a,eq}/L)} = \frac{\dfrac{x+1}{e^x} - 1}{(1 - e^{-x})\,(DU_{a,eq}/L)} < 0$$

Equation 1.3.30

hence $\underline{J_{tot} < J_{conv} + J_{dif}}$.

4. Unlike the approach developed for pollutant emission to the outdoor air, diffusive flux through the air boundary layer located at the soil surface is not taken into account here. This diffusive flux is not a limiting factor for pollutant emission due to the convective flux of air. It could only act as a control parameter, by checking that the soil between the source and the surface offers greater resistance to diffusion ($L/DU_{a,eq}$) than the air boundary layer (d_a/D_a). The equivalent diffusivity in each soil layer is always less than the diffusivity in air, except perhaps for substances with a Henry constant (H') less than 10^{-4} (but this model is applied essentially to volatile substances) and/or for a surface source ($L<d_a$: situation can equate to a volatile product present at the surface of a ground-level dwelling with a dirt floor, or a crawl space or dirt-floored cellar, following excavation in a deep source). In this second case, it would be necessary to consider attenuation of the source from the surface and the model presented here, based on the assumption of an infinite source, would no longer be appropriate.

5. Equation 1.3.26 assumes a low concentration in the soil air at the surface with the atmosphere compared to the concentration at the source. If this assumption is not confirmed, equation 1.3.26 overestimates J_{tot}. This tendency to overestimate can be limited by comparing $C_{as,n}$ to the background concentration in the air at the surface in gaseous form (cf. comment 3 in section 1.3.2.2).

1.3.1.1.4. CALCULATING THE AIR CONVECTIVE FLUX

The air flux through the vadose zone F_{is} is given by Darcy's law:

$$F_{is} = K_a \times \frac{\Delta p_{is}}{L}$$

Equation 1.3.31

Symbol	Parameters	Dimensions	Units	Status
F_{is}	Air flux from the soil to the building due to convection	$L.T^{-1}$	$m.s^{-1}$	C or E
K_a	Average air conductivity of the vadose zone (soil and/or floor)	$L^3.T.M^{-1}$	$m^3.s.kg^{-1}$	E
Δp_{is}	Pressure difference between the interior of the building (living area, basement or crawl space) and the soil	$M.L^{-1}.T^{-2}$	$kg.m^{-1}.s^{-2}$	E
L	Distance between the concentration point considered $C_{as}(L)$ and the interior of the building (living area, basement or crawl space)	L	m	E

1.3.1.1.4.1. AVERAGE AIR CONDUCTIVITY

When there are several superimposed layers, the average air conductivity is calculated as the harmonic mean of the conductivities of the different layers:

$$\frac{L}{K_a} = \sum_i \frac{l_i}{K_{a,i}}$$

Equation 1.3.32

hence $K_a = \dfrac{L}{\sum_i \dfrac{l_i}{K_{a,i}}}$

Equation 1.3.33

Symbol	Parameters	Dimensions	Units	Status
K_a	Average air conductivity of the vadose zone (soil and/or floor)	$L^3.T.M^{-1}$	$m^3.s.kg^{-1}$	C or E
L	Distance between the concentration point considered $C_{as}(L)$ and the interior of the building (living area, basement or crawl space)	L	m	C or E
$K_{a,i}$	Air conductivity of layer i	$L^3.T.M^{-1}$	$m^3.s.kg^{-1}$	C or E
l_i	Thickness of layer i	L	m	E

1.3.1.1.4.2. AIR CONDUCTIVITY OF A SOIL

The air conductivity of a soil is calculated from the air permeability of the soil and the viscosity of the air:

$$K_{a,i,sol} = \frac{\kappa_{int,i}}{\eta}$$

Equation 1.3.34

Symbol	Parameters	Dimensions	Units	Status
$K_{a,i,sol}$	Air conductivity of soil i	$L^3.T.M^{-1}$	$m^3.s.kg^{-1}$	C or E
$\kappa_{int,i}$	Air intrinsic permeability of soil i	L^2	m^2	C or E
η	Dynamic viscosity of air	$M.L^{-1}.T^{-2}$	$kg.m^{-1}.s^{-1}$	C or E

Values for air intrinsic permeability are given by different authors (cf. future documents on environmental parameters). The air permeability of a soil can also be estimated from the hydraulic conductivity.

1.3.1.1.4.3. AIR CONDUCTIVITY OF A FLOOR SLAB

The approach presented below was developed in the original VOLASOIL model (Waitz et al., 1996). In this model, openings in the concrete floor (gaps, cracks and holes) are represented as cylindrical tubes. The conductivity of the slab is then estimated by combining Poiseuille's and Darcy's laws.

For a cylindrical tube, length l and radius r, Poiseuille's law gives a laminar flux:

$$f = \frac{\pi \times r^4}{8 \times \eta} \times \frac{\Delta p}{l}$$

Equation 1.3.35

where η: dynamic viscosity of air,

    p: pressure.

For a column of length L, Darcy's law gives a flux:

$$F = K_a \times \frac{\Delta p}{L}$$

Equation 1.3.36

where K_a: air conductivity.

If n_i is the number of openings with radius i per unit area of the column, then

$$K_a \times \frac{\Delta p}{L} = \frac{\pi}{8 \times \eta} \times \frac{\Delta p}{l} \times \sum_i n_i \times r_i^4$$

Equation 1.3.37

hence $K_a = \frac{\pi}{8 \times \eta} \times \frac{L}{l} \times \sum_i n_i \times r_i^4$

Equation 1.3.38

and $K_a = \frac{\pi}{8 \times \eta \times \tau} \sum_i n_i \times r_i^4$

Equation 1.3.39

where τ: tortuosity,

$$\tau = \frac{l}{L}$$

Equation 1.3.40

Expression 1.3.39 is then included in VOLASOIL (Waitz et al., 1996) **by considering:**

- **vertical tubes, with tortuosity equal to 1,**
- **tubes of uniform radius r.**

Equation 1.3.39 thus leads to the following expression:

$$K_{a,pl} = \frac{f_{so} \times r^2}{8 \times \eta}$$

Equation 1.3.41

or $K_{a,pl} = \frac{f_{so}^2}{8 \times \eta \times \pi \times n_o}$

Equation 1.3.42

where f_{so}: surface area fraction of the floor slab occupied by the openings,

$$f_{so} = n_o \times \pi \times r^2$$

Equation 1.3.43

and n_o: number of openings in the floor slab per unit area

Symbol	Parameter	Dimensions	Units	Status
$K_{a,pl}$	Air conductivity of the floor slab	$L^3.T.M^{-1}$	$m^3.s.kg^{-1}$	C or E
r	Uniform radius of openings in the slab	L	m	C or E
f_{so}	Surface area fraction of the floor slab occupied by the openings	-	-	C or E
η	Dynamic viscosity of air	$M.L^{-1}.T^{-2}$	$kg.m^{-1}.s^{-1}$	E
n_o	Number of openings in the floor slab per unit area	L^{-2}	m^{-2}	E

Comments:

1. The choice of vertical tubes made in VOLASOIL, by reducing the distance to be covered by the air flux within the material, is conservative.

2. There is uncertainty associated with considering tubes with uniform radius. The flux in a tube is a function of r^4; if the orifices in the slab are of non-uniform size, it could cause significant variations in flux.

1.3.1.2. CONTAMINATED GROUNDWATER

When the contamination source is the groundwater, transfer across the capillary fringe can be considered.

The following equations provide a general solution for transfer through the capillary fringe. They take account of:

- a convective flux associated with evaporation,

- a diffusion flux in the air and in the water[7].

Locally, in the capillary fringe, evaporation flux is written as:

$$J_{conv\_cap} = E_v \times C_{es\_cap}$$

Equation 1.3.44

where $C_{es\_cap} = \dfrac{C_{as\_cap}}{H'}$

Equation 1.3.45

where J_{conv_cap}: evaporation flux in the capillary fringe,

E_v: evaporated water flow,

C_{es_cap}: concentration in the interstitial water of the capillary fringe,

C_{as_cap}: concentration in the air of the capillary fringe,

H': Henry constant (dimensionless).

With the diffusive flux described as before, the expression for total emission flux across the capillary fringe is written in the same way as derived for the vadose zone (cf. section 1.3.1.1.3), replacing:

- the convective flux of soil-air F_{is} by the convective flux of evaporation, converted to air-flux-equivalent, E_v/H';

- the concentration in soil air at the source in the vadose zone $C_{as,0}$ by the concentration in soil air at the surface of the groundwater C_{as_nap};

- the concentration in the soil air at the surface $C_{as,n}$ by the concentration in the soil air at the bottom of the vadose zone (limit of the capillary fringe) $C_{as,0}$;

- the depth of the source and equivalent multi-layer diffusivity in the vadose zone, L and $DU_{a,eq}$, by the thickness and equivalent multi-layer diffusivity of the capillary fringe, L_{cap} and DU_{eq_cap}.

The contaminant flux is then given by the following equation:

---

[7] The original VOLASOIL model does not take account of diffusion in air, considering that the high water content in the soil at the capillary fringe prevents any connection between residual air bubbles and therefore any continuous diffusion. The choice has been made here to present a complete expression of the diffusion flux. Ultimately, choice of parameters determines whether or not to select diffusion in air at the capillary fringe. Given the very low diffusivity in water compared to air, taking account of diffusion in air at the capillary fringe significantly increases diffusion.

$$J_{tot\_cap} = \frac{E_v}{H^{'}} \frac{C_{as\_nap} - e^{-\frac{Ev}{H^{'}} \frac{L_{cap}}{DU_{eq\_cap}}} C_{as,0}}{1 - e^{-\frac{Ev}{H^{'}} \frac{L_{cap}}{DU_{eq\_cap}}}}$$

Equation 1.3.46

where $C_{as\_nap} = H^{'} \times C_{e\_nap}$

Equation 1.3.47

where C_{e_nap}: dissolved concentration in the groundwater

Assuming steady state conditions and the principle of conservation of mass leads to equality of the flux passing through the soil (J_{tot}) and the flux crossing the capillary fringe (J_{tot_cap}),

hence $J_{tot} = \dfrac{E_v}{H^{'}} \dfrac{C_{as\_nap} - e^{-\frac{Ev}{H^{'}} \frac{L_{cap}}{DU_{eq\_cap}}} C_{as,0}}{1 - e^{-\frac{Ev}{H^{'}} \frac{L_{cap}}{DU_{eq\_cap}}}}$

Equation 1.3.48

If the pollutant is more volatile that water and in the absence of capillary rise as far as the surface with the atmosphere, $C_{as,0}$ is calculated from equations 1.3.24 and 1.3.46. Hence:

$$C_{as,0} = \frac{\dfrac{E_v}{H^{'}} \times \dfrac{C_{as\_nap}}{1 - e^{-\frac{Ev}{H^{'}} \frac{L_{cap}}{DU_{eq\_cap}}}} + \dfrac{F_{is} \times C_{as,n} \times e^{-F_{is} \times \frac{L}{DU_{a,eq}}}}{1 - e^{-F_{is} \times \frac{L}{DU_{a,eq}}}}}{\dfrac{F_{is}}{1 - e^{-F_{is} \times \frac{L}{DU_{a,eq}}}} + \dfrac{E_v}{H^{'}} \times \dfrac{e^{-\frac{Ev}{H^{'}} \frac{L_{cap}}{DU_{eq\_cap}}}}{1 - e^{-\frac{Ev}{H^{'}} \frac{L_{cap}}{DU_{eq\_cap}}}}}$$

Equation 1.3.49

If the concentration in the soil air at the surface with the atmosphere is low compared to that at the top of the capillary fringe, we consider that $C_{as,n} = 0$ and state:

$$C_{as,0} = \frac{\dfrac{E_v}{H^{'}} \times \dfrac{C_{as\_nap}}{1 - e^{-\frac{Ev}{H^{'}} \frac{L_{cap}}{DU_{eq\_cap}}}}}{\dfrac{F_{is}}{1 - e^{-F_{is} \times \frac{L}{DU_{a,eq}}}} + \dfrac{E_v}{H^{'}} \times \dfrac{e^{-\frac{Ev}{H^{'}} \frac{L_{cap}}{DU_{eq\_cap}}}}{1 - e^{-\frac{Ev}{H^{'}} \frac{L_{cap}}{DU_{eq\_cap}}}}}$$

Equation 1.3.50

Symbol	Parameters	Dimensions	Units	Status
J_{tot}	Gaseous pollutant flux at the surface of a building (for contaminated groundwater)	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
F_{is}	Air flux from the soil to the building due to convection	$L.T^{-1}$	$m.s^{-1}$	C or E
E_v	Evaporated water flow	$L.T^{-1}$	$m.s^{-1}$	C or E
H'	Henry constant (dimensionless): $H' = H/RT$	-	-	C or E
$C_{as,0}$	Pollutant concentration in the soil air, at the bottom of the vadose zone	$M.L^{-3}$	$mg.m^{-3}$	C or E
$C_{as,n}$	Pollutant concentration in the soil air at the surface (crawl space, basement or interior of the building)	$M.L^{-3}$	$mg.m^{-3}$	C or E
$C_{as,nap}$	Pollutant concentration in the soil air, at the surface of the groundwater	$M.L^{-3}$	$mg.m^{-3}$	C or E
L	Height of the transfer zone in the vadose zone, from the concentration point $C_{sa,0}$ to the interior of the building (crawl space or living area)	L	m	E
L_{cap}	Thickness of the capillary fringe	L	m	E
$DU_{a,eq}$	Average multiphase diffusion coefficient over the transfer zone considered, height L (expressed in relation to the concentration in the air)	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
DU_{eq_cap}	Average multiphase diffusion coefficient for the capillary fringe (expressed in relation to the concentration in the air)	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E

Comments:

1. To take account of any capillary rise as far as the surface (eg. in a cellar with beaten-earth floor), E_v/H' must be replaced by $F_{is} + E_v/H'$ in equation 1.3.48.

2. Estimating the concentration in water of the capillary fringe and groundwater using equations where $C_{w\_cap} = \frac{C_{as\_nap}}{H'}$ Equation *1.3.45* and where .... Equation 1.3.47, respectively, may correspond to a overestimating approach where multiphase equilibrium is assumed to have been reached.

3. As in section 1.3.1.1, the air boundary layer above the soil is not considered in equations 1.3.48 to 1.3.50.

4. Equation 1.3.50 assumes a low concentration in the soil air at the surface in contact with the atmosphere compared to the concentration in the soil air at the top of the capillary fringe. If this assumption is not confirmed,

$$C_{as,0} = \frac{\dfrac{E_v}{H'} \times \dfrac{C_{as\_nap}}{1 - e^{-\frac{Ev}{H'}\frac{L_{cap}}{DU_{eq\_cap}}}}}{\dfrac{F_{is}}{1 - e^{-F_{is} \times \frac{L}{DU_{a,eq}}}} + \dfrac{E_v}{H'} \times \dfrac{e^{-\frac{Ev}{H'}\frac{L_{cap}}{DU_{eq\_cap}}}}{1 - e^{-\frac{Ev}{H'}\frac{L_{cap}}{DU_{eq\_cap}}}}}$$

Equation 1.*3.50* overestimates J_{tot}. This tendency to overestimate can be limited by assimilating $C_{as,n}$ to the background concentration in the air at the surface (cf. comment 3 in section 1.3.2.2).

5. For a submerged pollutant source (eg. pollutant more dense than water) and a 'badly-mixed' aquifer, transfer in the groundwater must be considered. In this case, transfer flow will be estimated by considering the saturated zone as an additional layer (without air) of the capillary fringe and by including diffusion in the groundwater in the model.

To do so, in equations 1.3.46 to 1.3.50,

- the diffusion coefficient DU_{eq_cap} is replaced by a multi-layer diffusion coefficient $DU_{eq\_cap\_nap}$ including the diffusion coefficient in the groundwater according to the principle of equation 1.2.21 (resistance of all layers equals the sum of resistances of all the layers);
- the thicknesses of the capillary fringe L_{cap} is replaced by the sum of thicknesses of the capillary fringe and the groundwater to be crossed, L_{cap_nap}.

1.3.1.3. IMPACT OF ASSUMPTIONS UNDERPINNING THE MODEL

The model developed here does not take account of degradation of pollutants during transfer from the source. This assumption is conservative. But it must be particularly remembered that it does not take into account attenuation of the pollutant at the source over time (chemical or biological transformations, leaching, volatilisation, etc.), which amounts to considering an infinite source. This assumption can lead to a significant overestimate if the source is just beneath the slab or only at shallow depth, if the soil is very permeable or if the substance studied is very volatile.

Furthermore the model assumes that the convective flux passes through the whole vadose zone from the pollution source in the soil, under the effect of the pressure difference between the soil and the interior of the building. This implies that air extracted from the soil, and that comes initially from the surface, passes through the vadose zone (as shown by the arrows in the figure below), passing through the pollution source, without a short-circuit from the overlying soil, particularly from the subgrade (gravel) under the slab. For a capillary fringe or a deep soil, this assumption appears unrealistic. This conceptual limit implies that the model is very conservative for sources at great depths. In these situations, vapour emissions may be limited by diffusion below the zone affected by convection[8]. For permeable soils, convection may represent 99% of the calculated flux, hence overestimating the flux by up to two orders of magnitude.

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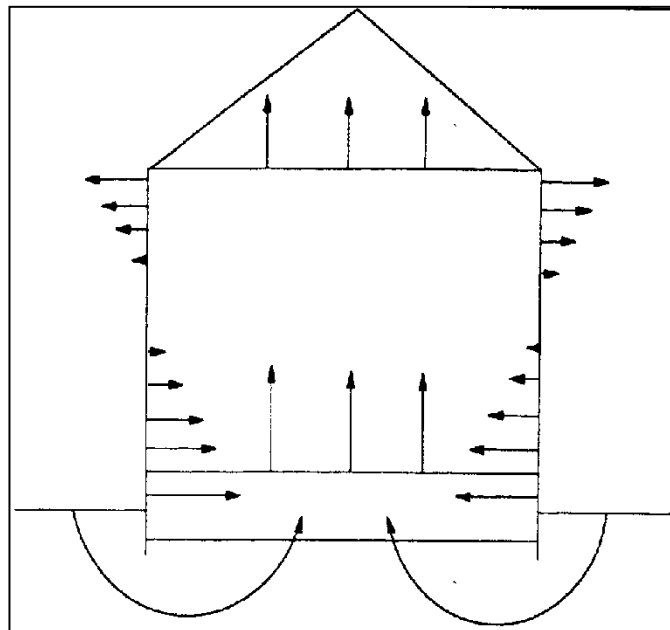
[8] Convection in the mixing zone will stimulate this underlying diffusion, since it will reduce concentrations at the edge of this zone.

Figure 8: Convective transport of air in a house (Waitz et al., 1996)

Two comments can be made about diffusion fluxes in the soil:

- estimating diffusion coefficients in the soil that consider the whole porosity of the soil useful for diffusion may lead to overestimations where the soil conductivity is obstructed. In this case, it could be appropriate to use the effective porosity. However, laboratory diffusion tests with inert gases (van den Berg, 1994 and Waitz et al., 1996, US EPA, 1994), show that these formulae match the best available knowledge and fit well with reality. According to Waitz et al. (1996), they can slightly underestimate diffusion coefficient for soil with a low air content, which is not the case of the soils considered here;

- the above model takes account of diffusion in the air of the capillary fringe, which tends to significantly increase the diffusion flux from the water table compared to the original model. It may prove too conservative to take this diffusion flux in air at the capillary fringe into account, because a high water content can prevent any continuous diffusion at the capillary fringe and because, under these conditions, pollutant diffusion across the capillary fringe may be greater than the ability of the groundwater to maintain the supply (hence depleting the pollutant concentration in the air at the water table). The influence of taking account of diffusion in the air at the capillary fringe can be studied by varying the value assigned to the air content in the capillary fringe.

Finally, selecting parameters for cracking of the slab appears very uncertain. VOLASOIL uses an average crack radius of 4 mm. This value for the parameter is often considered excessive. However, no measurement of this conductivity provides a result and suggests an alternative value for this parameter.

The VOLASOIL model, like other vapour transfer models, has undergone little experimental validation work (Swartjes, 2003a, Waitz et al., 1996, appendix 6). Waitz et al. (1996) reports comparisons between simulations and measurements from contamination of groundwater. Concentrations modelled in the crawl space appear to be consistently overestimated, by a factor of 5 to 300. An experiment conducted by INERIS as part of its research projects also resulted in measurements (repeated but not systematic) of a pollutant flux through a slab on an industrial site 50 to 1000 times greater than the values predicted with the VOLASOIL model (with conservative parameter values compared to data from the site).

Given these uncertainties and the little available confirming information, modelling vapour transfer, whether using VOLASOIL or another model, is c particularly uncertain for the moment. An uncertainty of about two orders of magnitude is proposed in Europe (Swartjes, 2003b). Such an order of magnitude seems consistent with the scale of variations observed between models or during the few experimental verification tests carried out.

1.3.2. GASEOUS POLLUTANT CONCENTRATION IN THE INDOOR AIR

The inhabited part of a building rests:

- either on a slab sitting on the soil: this is called 'slab-on-grade',
- or on a crawl space,
- or on a basement.

In the first case, the building slab can be compared to a soil layer and the multi-layer transfer model can be used to calculate the pollutant flux emitted into the living area after passing through the soil and the slab. The concentration in the indoor air is then calculated from this flux.

In the case of a crawl space or a basement, pollutant vapours passing through the soil (and the slab making up the basement floor) can be diluted in the crawl space or basement before reaching the living area.

1.3.2.1. GASEOUS POLLUTANT CONCENTRATION IN THE ZONE OF THE BUILDING WHERE THE EMISSION OCCURRED

The gaseous pollutant concentration attributable to the soil or groundwater source, in the zone of the building ($C_{ag\_bât}$) where the emission occurred, is calculated from the flux at the surface of the building and the following mass balance:

$$V_{bât} \times \frac{dC_{ag\_bât}}{dt} = J_{tot} \times A_{bât} + t_{ra} \times V_{bât} \times C_{ag,e} - (F_{is} \times A_{bât} + t_{ra} \times V_{bât}) \times C_{ag\_bât}$$ Equation 1.3.51

where $A_{bât}$: surface area of the building,

t_{ra}: air renewal rate in the building,

$V_{bât}$: interior volume of the building where the emission of gaseous pollution occurred, from the soil or the capillary fringe,

$C_{ag,e}$: pollutant concentration in gaseous form in the outdoor air, attributable to the source studied.

Integrating equation 1.3.51 over time intervals (ΔT) where J_{tot}, F_{is}, t_{ra} and $C_{ag,e}$ are constant gives:

$$C_{ag\_bât}(t) = \frac{J_{tot} + t_{ra} \times H_{bât} \times C_{ag,e}}{F_{is} + t_{ra} \times H_{bât}} \times \left(1 - e^{-\left(\frac{F_{is}}{H_{bât}} + t_{ra}\right)\Delta T} \right) + C_{ag\_bât}(t - \Delta T) \times e^{-\left(\frac{F_{is}}{H_{bât}} + t_{ra}\right)\Delta T}$$

Equation 1.3.52

Comment: over long periods, it is possible to take account of variations in emission flux (eg. due to temperature variations with the seasons). The variations considered must nonetheless be sufficiently infrequent to be compatible with the assumed equality of fluxes between the different soil layers, used to define the expression for J_{tot}.

If J_{tot}, F_{is}, t_{ra} and $C_{ag,e}$ are constant throughout the period studied, it can be stated:

$$C_{ag\_bât}(t) = \frac{J_{tot} + t_{ra} \times H_{bât} \times C_{ag,e}}{F_{is} + t_{ra} \times H_{bât}} \times \left(1 - e^{-\left(\frac{F_{is}}{H_{bât}} + t_{ra}\right)t} \right) + C_{ag\_bât}(0) \times e^{-\left(\frac{F_{is}}{H_{bât}} + t_{ra}\right)t}$$ Equation 1.3.53

When steady state conditions are achieved:

$$C_{ag\_bât} = \frac{J_{tot} + t_{ra} \times H_{bât} \times C_{ag,e}}{F_{is} + t_{ra} \times H_{bât}}$$ Equation 1.3.54

Symbol	Parameter	Dimensions	Units	Status
$C_{ag\_bât}$	Gaseous pollutant concentration, attributable to the soil or groundwater source, in the air of the building zone where the emission occurred	$M.L^{-3}$	$mg.m^{-3}$	C or E
$C_{ag,e}$	Gaseous pollutant concentration in the outdoor air, attributable to the soil or groundwater source	$M.L^{-3}$	$mg.m^{-3}$	C or E
F_{is}	Air flux from the soil to the building due to convection	$L.T^{-1}$	$m.s^{-1}$	C or E
J_{tot}	Gaseous pollutant flux at the surface of the building	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
t_{ra}	Ventilation coefficient of the living area, crawl space or basement of the building, as appropriate (= air renewal rate)	T^{-1}	s^{-1}	E
$H_{bât}$	Height of the space considered (living area, crawl space or basement of the building, as appropriate)	L	m	E

1.3.2.2. GASEOUS POLLUTANT CONCENTRATION IN THE AIR OF THE LIVING AREA

If the floor of the building rests directly on the soil, the gaseous pollutant concentration attributable to the soil or groundwater source in the air of the living area ($C_{ag,i}$) is given by equations 1.3.52, 1.3.53. or 1.3.54.

For a building over a crawl space or basement, the gaseous pollutant concentration in the living area depends on the pollutant concentration in the crawl space or basement, as appropriate, and the vapour transfer between these two spaces. Several approaches are therefore possible to estimate the gaseous concentration in the indoor air of the inhabited area of a building:

- vapour transfer is modelled. Thus, in the original VOLASOIL model Waitz et al. (1996) represent this transfer by a convective flux generated by the pressure difference between the crawl space and the living area. The air flux entering the living area from the crawl space is estimated from existing openings in the floor of the inhabited part (cf. section 1.3.1.1.4.3);

- an empirical dilution factor is used, as in HESP (Human Exposure to Soil Pollutants: Veerkamp and ten Berge, 1994, Shell Global Solutions, 1995) or CSOIL (van den Berg R., 1994). The gaseous pollutant concentration in the basement or crawl space is then multiplied by this factor to obtain the gaseous pollutant concentration in the air of the living area.

To calculate gaseous pollutant concentrations in the air of the living area of a building, INERIS favours the second approach, basing calculations on measurement data to define the dilution coefficient. Even if the value of this parameter can be variable and uncertain, this approach has been chosen because:

- the VOLASOIL calculation model to estimate vapour transfer from the crawl space to the basement has not been compared with measurements,

- the density and large variability in the size of orifices in the concrete slab (cracks, conduits, etc.), which determine the conductivity to convective flux, cannot be measured and are not justified in the VOLASOIL reference documentation (INERIS, DRC-05-57281-DESP/R01a).

Thus, the gaseous pollutant concentration in the indoor air, attributable to pollution of the soil, is given by:

$$C_{ag,i} = C_{ag\_bât} \times f_{d\_sb}$$

<div align="right">Equation 1.3.55</div>

This equation assumes that **exchanges between the living area and the crawl space or basement are sufficiently rapid that variations in C$_{ag\_bât}$ are reflected in C$_{ag,i}$.**

Symbol	Parameter	Dimensions	Units	Status
C$_{ag,i}$	Gaseous pollutant concentration, attributable to the soil or groundwater source, in the air of the living area of a building over a crawl space or basement	M.L^{-3}	mg.m^{-3}	C or E
C$_{ag\_bât}$	Gaseous pollutant concentration in the air of the crawl space or basement, attributable to the soil or groundwater source	M.L^{-3}	mg.m^{-3}	C or E
f$_{d\_sb}$	Contribution of air in the crawl space or basement to the indoor air of the living area	-	-	E

Comments:

1. For a building where the floor of the living area rests on the soil, expression 1.3.55 can be used with f$_{d\_sb}$ equal to 1.

2. The expressions given above relate to gaseous pollutant concentrations in the air attributable to the soil or groundwater source. They do not include the background concentration in the air of the living area, crawl space or basement and other pollution sources present in these places.

3. The gaseous concentration in the air of the building is calculated from mass balance 1.3.51 using the emission flux J$_{tot}$ attributable to the source. This flux must therefore be estimated from the concentration in the soil air at the source, without taking account of the background concentration.

   In reality, the net diffusion flux depends on the difference between the total pollutant concentration in the soil air at the source and the total concentration in the soil air at the soil surface. As a result, the attributable concentration and the total concentration at the source can be considered as almost the same for contamination of soils or groundwater by volatile or semi-volatile compounds (cases where these equations can be used). Conversely, the concentration in the air of the building or living area can, for certain pollutants (such as benzene, toluene, formaldehyde) can be relatively high. In this case, given the calculation assumptions (concentration in soil air at the surface low compared to the concentration in the soil air at the source for a soil source or at the top of the capillary fringe for a groundwater source), using equations 1.3.26 and 1.3.50 can lead to overestimating the emission flux J$_{tot}$ and the concentration in the air of the building attributable to the soil source of groundwater source.

   To limit this tendency to overestimate, it is possible to compare the concentration in the soil air at the surface C$_{as,n}$ to the background concentration in gaseous form in the air of the living area, crawl space or basement (as appropriate), in equations 1.3.24 and 1.3.49 (the diffusion flux in the air boundary layer at the soil surface is not taken into account and the concentration in the soil air at the surface, attributable to the source, being again considered negligible).

Conversely, if the background concentration in gaseous form in the air of the living area, crawl space or base (as appropriate) is greater than or equal to the concentration in the soil air at the source and if the convective flux is negligible, then the concentration in the air attributable to the soil or groundwater source will be considered as zero.

4. The total gaseous pollutant concentration in a living area where the floor rests directly on the soil, in a crawl space or basement, is then obtained by adding the background concentration in gaseous form measured in these media (cf. section 4) to expressions 1.3.52, 1.3.53 or 1.3.54.

The total gaseous pollutant concentration in the air of the living area of a building constructed over a crawl space or basement is obtained by adding the measured background concentration in gaseous form in the dwelling to equation 1.3.55 ($C_{ag\_bât}$ used in this equation is the gaseous pollutant concentration attributable to the source studied).

1.4. 'GROUNDWATER' MEDIUM

1.4.1. DISPERSION IN THE GROUNDWATER

The principal mechanisms associated with the propagation of pollutants in aquifers (comprising a saturated zone – groundwater – and vadose zone) are:

- convection,
- kinematic dispersion,
- molecular diffusion,
- adsorption,
- biodegradation,
- volatilisation.

These mechanisms depend on numerous factors associated with the characteristics of the medium and the pollutants considered, such as:

- flow, associated with the nature of the underground medium (porous, cracked or karstic; whether or not to consider the vadose zone), as well as conditions at the boundaries of the system (climatic variations, flow rate of water courses, etc.);

- the presence of organic matter cause a delayed effect, due to sorption of a pollutant to it;

- the presence of bacteria likely to break down these pollutants;

- behaviour of the pollutants (tracer-substance – whether or not chloride, miscible or immiscible in water, volatile or non-volatile). Some immiscible chemicals (soluble to some degree) denser than water will tend to migrate to the bottom of the groundwater (as far as the impermeable substratum) as illustrated in Figure 9, while others less dense than water will be 'supernatants' (cf. Figure 10).
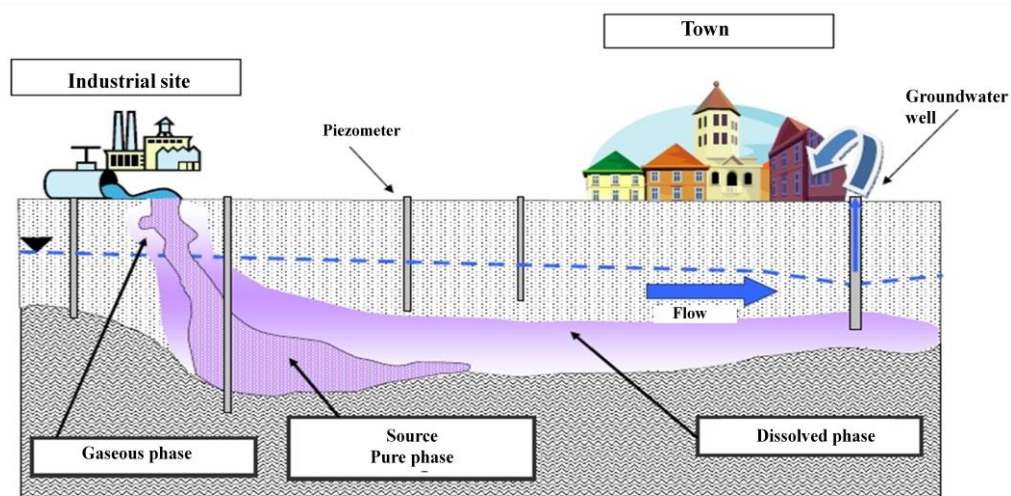
Figure 9: Behaviour of a chemical for which the pure phase is denser than water (such as tetrachloroethylene)
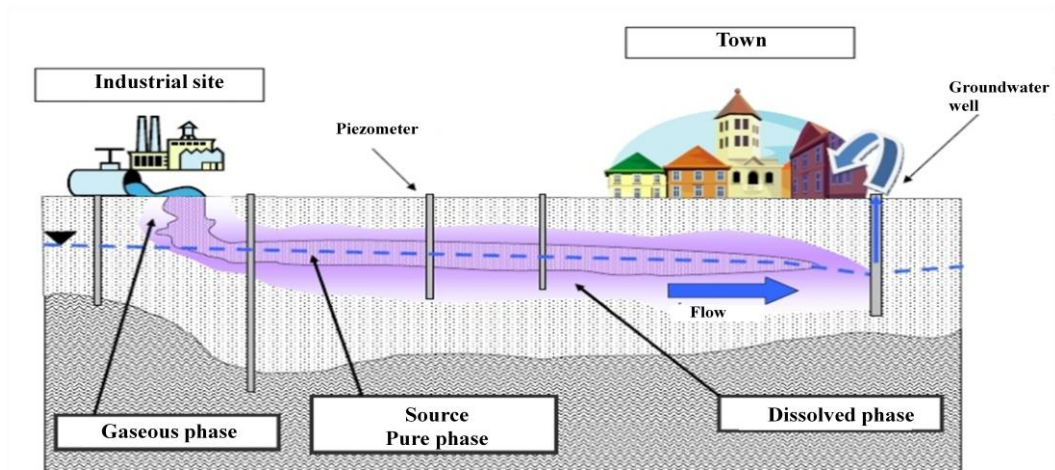
Figure 10 : Behaviour of a chemical for which the pure phase is less dense than water (such as benzene)

In practice, the porous medium represents the very great majority of cases covered as part of risk studies associated with facilities, whether or not they are operating. Two explanations can be suggested:

- potentially polluting facilities (registered facilities in particular) are generally sited alongside water courses (alluvial aquifers, which are porous media);
- other media (cracked and karstic) are covered as part of research projects, and by simplification we are considering a porous medium. In fact, simulating the transfer (flow and transport) is more complex in these media (cracked and karstic).

Furthermore, during transfer within groundwater, exchanges are likely to take place with other media. Degassing from saturated zone to the vadose zone of an aquifer can lead to volatile pollutants migrating, via the soil gas, to the atmosphere (cf. section 1.2.2.2) or a dwelling (indoor air, cf. section 1.3.1.2). Relationships with the drainage system (called 'groundwater/river exchange') can also result in migration between groundwater and surface water.

Exchanges can also occur with the matrix, for example, between clays and metals. This is referred to as reactive transport.

These transfers between media and with the matrix are difficult to simulate, because it means using calculation tools that require a lot of input data, very often unknown or subject to significant uncertainties regarding the applicability to the case in question.

Modelling all the mechanisms and interactions therefore remains very complex, although there is now a wide variety of calculation tools, from the most simplified (analytical models) to the most sophisticated (numerical models) to evaluate the transfer of pollutants in groundwater.

This section on modelling the transport of pollutants in groundwater presents basic equations for flow in a saturated medium, the general equation for transport of pollutants in dissolved phase and saturated medium (without volatilisation), as well as the simplified analytical solution developed by Domenico to simulate the transport of pollutants. Other models are also listed and the general approach to modelling is summarised. This section therefore comprises only an introduction to modelling in a saturated medium. Its purpose is to provide risk assessors with basic information and enable them to talk to specialists with more detailed tools for dealing with more complex situations.

1.4.1.1. GROUNDWATER FLOW

1.4.1.1.1. BASIC FLOW EQUATION (DARCY'S EQUATION)

Darcy's law, established experimentally (for a porous medium) by Darcy in 1856, is the basis of underground hydrodynamics. It is expressed as follows:

$$Q = K_e.A.\frac{\Delta h}{l}$$

Equation 1.4.1

where Q: hydraulic flow rate,

K_e: hydraulic conductivity,

A: total surface area of the cross-section perpendicular to flow,

Δh: load variation,

l: length.

The load variation over the length defines the hydraulic gradient i (dimensionless):

$$\frac{\Delta h}{l} = i$$

Equation 1.4.2

and the flow rate over the area of the cross-section corresponds to the filtration velocity or Darcy velocity:

$$\frac{Q}{A} = K_e \times i = v_d$$

Equation 1.4.3

Symbol	Parameters	Dimensions	Units	Status
v_d	Filtration or Darcy velocity	$L.T^{-1}$	$m.s^{-1}$	C or E
i	Hydraulic gradient	-	-	C or E
Q	Hydraulic flow rate	$L^3.T^{-1}$	$m^3.s^{-1}$	C or E
K_e	Hydraulic conductivity	$L.T^{-1}$	$m.s^{-1}$	C or E
A	Total surface area of the cross-section, perpendicular to flow	L^2	m^2	E
Δh	Load variation	L	m	E
l	Length	L	m	E

The conditions under which this law is valid are: continuity, isotropy, homogeneity of the reservoir and laminar flow. In practice, although these conditions are very restrictive, cases where this law is no longer applicable are limited to very heterogeneous formations, karstic systems, when the velocity is very high, such as close to a pumping system.

Strictly speaking, the hydraulic conductivity (K_e) is associated with both the properties of the medium (air permeability κ_{int}) and those of the fluid (density and dynamic viscosity). For shallow groundwater sources (< 1000 m), with low pressure and temperature, and low concentrations of dissolved salts, the effects of viscosity and density can be neglected.

Consequently, the Darcy equation has been generalised (Magnan). It can be stated:

$$\vec{v}_d = -K_e \cdot \overrightarrow{gradh}$$ Equation 1.4.4

1.4.1.1.2. SIMPLIFIED APPROACH TO ESTIMATE THE TRANSFER VELOCITY AND TIME

As a first approach, it is possible to evaluate the transfer time of (dissolved) chemical in a saturated zone by considering the Darcy velocity (v_d). This approach is conservative, because three phenomena are not considered:

- the transfer time in a vadose zone,
- the delay potentially caused by the sorption phenomenon,
- potential transformation via degradation or biodegradation.

In order to take account of the fact that only gravitational water is moving (particularly, unlike bound water between the pores) and that only an effective surface area contributes to flows, filtration velocity is corrected by the effective porosity:

$$v_e = \frac{K_e.i}{n_e}$$ Equation 1.4.5

Symbol	Parameters	Dimensions	Units	Status
v_e	Effective velocity	$L.T^{-1}$	$m.s^{-1}$	C or E
K_e	Hydraulic conductivity	$L.T^{-1}$	$m.s^{-1}$	C or E
i	Hydraulic gradient	-	-	C or E
n_e	Effective porosity (gravity-fed water volume/total volume)	-	-	E

Comment: the effective velocity (v_e) approaches the movement velocity measured in the field (actual velocity approached by *in situ* tracking).

The relationship that links velocity to time can be used to calculate a transfer time as a function of distance:

$$T_{transfert} = \frac{d_{source \rightarrow point}}{v_e}$$ Equation 1.4.6

Symbol	Parameters	Dimensions	Units	Status
$T_{transfert}$	Transfer time between the source and downstream point considered	T	s	C or E
v_e	Effective velocity	$L.T^{-1}$	$m.s^{-1}$	C or E
$d_{source \rightarrow point}$	Distance between the source and downstream point	L	m	E

1.4.1.2. TRANSPORT OF POLLUTANTS IN DISSOLVED PHASE AND SATURATED MEDIUM

The transport equation defining the concentration variations as a function of time in an aquifer derives from the principle of mass conservation. If in a homogeneous porous medium, **we consider a unidirectional flow and dispersion mechanisms in three dimensions**, we can state for a differential volume (dV = dx.dy.dz):

$$n_e . \frac{\partial C_{e\_nap}}{\partial t} + (n_{aq} - n_e) . \frac{\partial C'_{e\_nap}}{\partial t} + MV_{aq} . \frac{\partial C_{aq\_ads}}{\partial t} =$$

$$n_e . (D_{eff,x} . \frac{\partial^2 C_{e\_nap}}{\partial x^2} + D_{eff,y} . \frac{\partial^2 C_{e\_nap}}{\partial y^2} + D_{eff,z} . \frac{\partial^2 C_{e\_nap}}{\partial z^2})$$

$$+ (n_{aq} - n_e) . \left(D_{e,aq} . \frac{\partial^2 C'_{e\_nap}}{\partial x^2} + D_{e,aq} . \frac{\partial^2 C'_{e\_nap}}{\partial y^2} + D_{e,aq} . \frac{\partial^2 C'_{e\_nap}}{\partial z^2} \right)$$

$$- n_e . v_e \times \frac{\delta C_{e\_nap}}{\delta x} - \lambda_{aq} . \left[n_e . C_{e\_nap} + (n_{aq} - n_e) . C'_{e\_nap} + MV_{aq} . C_{aq\_ads} \right]$$

Equation 1.4.7

where C_{e_nap}: pollutant concentration per unit volume in the mobile phase of the water,

C'_{e_nap}: pollutant concentration per unit volume in the immobile phase of the water,

C_{aq_ads}: pollutant concentration per unit mass on the solid phase,

MV_{aq}: bulk density of the aquifer,

λ_{aq}: degradation coefficient of the pollutant in the saturated zone,

n_{aq}: total porosity of the aquifer,

n_e: effective porosity,

v_e: effective velocity or pore velocity,

$D_{eff,x}$, $D_{eff,y}$, $D_{eff,z}$: effective dispersion coefficient in x, y and z directions (cf. section 1.4.1.2.1),

$D_{e,aq}$: molecular diffusion coefficient (cf. section 1.4.1.2.3).

1. If the **pollutant concentration in the immobile phase of the water (C'_{e_nap}) is close to the concentration in the mobile phase (C_{e_nap}) (significant diffusion)**, equation 1.4.7 is written:

$$n_{aq} . \frac{\partial C_{e\_nap}}{\partial t} + MV_{aq} . \frac{\partial C_{aq\_ads}}{\partial t} = n_{aq} . (D_{eff,x} . \frac{\partial^2 C_{e\_nap}}{\partial x^2} + D_{eff,y} . \frac{\partial^2 C_{e\_nap}}{\partial y^2} + D_{eff,z} . \frac{\partial^2 C_{e\_nap}}{\partial z^2})$$

$$- n_e . v_e \times \frac{\delta C_{e\_nap}}{\delta x} - \lambda_{aq} . \left[n_{aq} . C_{e\_nap} + MV_{aq} . C_{aq\_ads} \right]$$

Equation 1.4.8

If the pollutant is adsorbed onto particles in the aquifer, if the multiphase equilibrium is reached and if adsorption can be described by the partition coefficient (K_{d_aq}), equation 1.4.8 becomes:

$$\frac{\partial C_{e\_nap}}{\partial t} = \frac{D_{eff,x}}{R} \times \frac{\partial^2 C_{e\_nap}}{\partial x^2} + \frac{D_{eff,y}}{R} \times \frac{\partial^2 C_{e\_nap}}{\partial y^2} + \frac{D_{eff,z}}{R} \times \frac{\partial^2 C_{e\_nap}}{\partial z^2}$$

$$- \frac{v_d}{n_{aq}.R} \times \frac{\delta C_{e\_nap}}{\delta x} - \lambda_{aq} \times C_{e\_nap}$$

Equation 1.4.9

where v_d: Darcy velocity,

R: delay coefficient:

$$R = 1 + \frac{MV_{aq} \times K_{d\_aq}}{n_{aq}}$$

Equation 1.4.10

2. If the **pollutant concentration in the immobile phase of the water (C'_{e_aq}) is close to zero (negligible diffusion)**, equation 1.4.7 is written:

$$n_e.\frac{\partial C_{e\_nap}}{\partial t} + MV_{aq}.\frac{\partial C_{aq\_ads}}{\partial t} = n_e.(D_{eff,x}.\frac{\partial^2 C_{e\_nap}}{\partial x^2} + D_{eff,y}.\frac{\partial^2 C_{e\_nap}}{\partial y^2}$$

$$+ D_{eff,z}.\frac{\partial^2 C_{e\_nap}}{\partial z^2})$$

$$- n_e.v_e \times \frac{\delta C_{e\_nap}}{\delta x} - \lambda_{aq}.\left[n_e.C_{e\_nap} + MV_{aq}.C_{aq\_ads} \right]$$

Equation 1.4.11

If the pollutant is adsorbed onto particles in the aquifer, if the multiphase equilibrium is reached and if adsorption can be described by the partition coefficient (K_{d_aq}), equation 1.4.11 becomes:

$$\frac{\partial C_{e\_nap}}{\partial t} = \frac{D_{eff,x}}{R} \times \frac{\partial^2 C_{e\_nap}}{\partial x^2} + \frac{D_{eff,y}}{R} \times \frac{\partial^2 C_{e\_nap}}{\partial y^2} + \frac{D_{eff,z}}{R} \times \frac{\partial^2 C_{e\_nap}}{\partial z^2}$$

$$- \frac{v_e}{R} \times \frac{\delta C_{e\_nap}}{\delta x} - \lambda_{aq} \times C_{e\_nap}$$

Equation 1.4.12

where $R = 1 + \dfrac{MV_{aq} \times K_{d\_aq}}{n_e}$ Equation 1.4.13

Comment: If total porosity (n_{aq}) is almost the same as the kinematic porosity (n_e), equations 1.4.8, 1.4.9 and 1.4.10 are equivalent, respectively, to equations 1.4.11, 1.4.12 and 1.4.13.

Reminder: **Pollutant loss by volatilisation from the water table is not considered in this approach.**

1.4.1.2.1. ESTIMATING EFFECTIVE DISPERSION COEFFICIENTS

The effective dispersion coefficient represents the molecular diffusion and kinematic dispersion mechanisms for the pollutant in liquid phase. Molecular diffusion is associated to the Brownian motion of molecules in solution. Kinematic (or dynamic) dispersion depends on the heterogeneity of the porous medium. This heterogeneity is manifested as random dispersion of actual velocities of the water particles around the average movement velocity of the water.

Effective dispersion coefficients are equal to:

$$D_{eff,x} = D_{isp,x} + D_{e,aq}$$
Equation 1.4.14

$$D_{eff,y} = D_{isp,y} + D_{e,aq}$$
Equation 1.4.15

$$D_{eff,z} = D_{isp,z} + D_{e,aq}$$
Equation 1.4.16

Symbol	Parameters	Dimensions	Units	Status
$D_{eff,x}$, $D_{eff,y}$, $D_{eff,z}$	Effective dispersion coefficients in x, y and z directions	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
$D_{isp,x}$, $D_{isp,y}$, $D_{isp,z}$	Kinematic dispersion coefficients in x, y and z directions	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
$D_{e,aq}$	Molecular diffusion coefficient of the pollutant in the water in the saturated zone	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E

1.4.1.2.2. ESTIMATING KINEMATIC DISPERSION COEFFICIENTS

Kinematic dispersion coefficients are given by the following relationships:

1. $$D_{isp,x} = \alpha_L \times v_e$$
Equation 1.4.17

where v_e: effective velocity,

α_L: longitudinal dispersivity:

$$\alpha_L = 0,1 \times L_p$$
Equation 1.4.18

where L_p: plume length,

2. $$D_{isp,y} = \alpha_T \times v_e$$
Equation 1.4.19

where α_T: transverse dispersivity. It is assumed to represent $1/10^{th}$ of the longitudinal dispersivity.

3. $$D_{isp,z} = \alpha_v \times v_e$$
Equation 1.4.20

where α_v: vertical dispersivity. Vertical dispersivity can generally be neglected, because it is very low. In addition, as a first approach, the source is conventionally allocated to the entire saturated zone and this parameter no longer has a place.

Dispersivity can be determined *in situ* by tracking.

Symbol	Parameters	Dimensions	Units	Status
$D_{isp,x}$	Longitudinal kinematic dispersion coefficient	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
$D_{isp,y}$	Transverse kinematic dispersion coefficient	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
$D_{isp,z}$	Vertical kinematic dispersion coefficient	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
α_L	Longitudinal dispersivity	L	m	C or E
α_T	Transverse dispersivity	L	m	C or E
α_v	Vertical dispersivity	L	m	C or E
v_e	Effective velocity	$L.T^{-1}$	$m.s^{-1}$	C or E
L_p	Plume length	L	m	E

1.4.1.2.3. ESTIMATING THE MOLECULAR DIFFUSION COEFFICIENT IN THE GROUNDWATER

According to Millington and Quirk (1961), the molecular diffusion coefficient in the groundwater $D_{e,aq}$ is given by:

$$D_{e,aq} = D_e \times \tau_{aq}$$

Equation 1.4.21

where $\tau_{aq} = \dfrac{\theta_{aq}^{\frac{10}{3}}}{n_{aq}^2} = n_{aq}^{\frac{4}{3}}$

Equation 1.4.22

Symbol	Parameters	Dimensions	Units	Status
$D_{e,aq}$	Molecular diffusion coefficient of the pollutant in the water in the saturated zone	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
D_e	Molecular diffusion coefficient of the pollutant in water	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
τ_{aq}	Tortuosity coefficient in the aquifer	-	-	C or E
n_{aq}	Porosity of the aquifer	-	-	E

Comment: In porous media, molecular diffusion can be negligible compared to dispersion. In fact, it only has a role at low flow velocities (<=10 cm/d) or over very long periods of time (eg. studies conducted on storage of high activity wastes in deep geological layers and with very low permeability).

1.4.1.3. DOMENICO'S SOLUTION

Domenico (1985, 1987) proposed a simplified solution to equation 1.4.7, representing the transport of pollutants in saturated media and dissolved phase, which is taken as it is or adapted in numerous analytical models.

The following expression gives the modified Domenico solution for a surface pollutant source in the saturated zone, perpendicular to flow, between (-Y_{source_aq} / 2; +Y_{source_aq} / 2) and (-Z_{source_aq} / 2; +Z_{source_aq} / 2) and constant concentration $C_{e\_nap,0}$. This expression, identical to that in the publication by West et al, (2007, equation 22), is obtained with the following initial conditions:

$C_{e\_nap}(x, y, z, 0) = 0$ (zero initial concentration for x, y, z >0)

and $C_{e\_nap}(0, y, z, 0) = C_{e\_nap,0}$ (concentration equals $C_{e\_nap,0}$ at the initial instant at the source),

$$C_{e\_nap}(x, y, z, t) = \frac{C_{e\_nap,0}}{8} \times f_x \times f_y \times f_z$$

Equation 1.4.23

$$f_x = \exp\left(\frac{v_d^{'}.x}{2.D_{eff,x}} \cdot \left(1 - \sqrt{1 + \frac{4.\lambda_{aq}.R.D_{eff,x}}{\left(v_d^{'}\right)^2}}\right)\right).erfc\left(\frac{x - \frac{v_d^{'}}{R}.t.\sqrt{1 + \frac{4.\lambda_{aq}.R.D_{eff,x}}{\left(v_d^{'}\right)^2}}}{2.\sqrt{\frac{D_{eff,x}}{R}.t}}\right)$$

where

$$+ \exp\left(\frac{v_d^{'}.x}{2.D_{eff,x}} \cdot \left(1 + \sqrt{1 + \frac{4.\lambda_{aq}.R.D_{eff,x}}{\left(v_d^{'}\right)^2}}\right)\right) \times erfc\left(\frac{x + \frac{v_d^{'}}{R}.t.\sqrt{1 + \frac{4.\lambda_{aq}.R.D_{eff,x}}{\left(v_d^{'}\right)^2}}}{2.\sqrt{\frac{D_{eff,x}}{R}.t}}\right)$$

Equation 1.4.24

$$f_y = erf\left(\frac{y + Y_{source\_aq}/2}{2.\sqrt{\frac{D_{eff,y} \cdot x}{v_d^{'}}}}\right) - erf\left(\frac{y - Y_{source\_aq}/2}{2.\sqrt{\frac{D_{eff,y} \cdot x}{v_d^{'}}}}\right)$$

Equation 1.4.25

$$f_z = erf\left(\frac{z + Z_{source\_aq}/2}{2.\sqrt{\frac{D_{eff,z} \cdot x}{v_d^{'}}}}\right) - erf\left(\frac{z - Z_{source\_aq}/2}{2.\sqrt{\frac{D_{eff,z} \cdot x}{v_d^{'}}}}\right)$$

Equation 1.4.26

Depending on the case, (cf. section 1.4.1.2),

we obtain: $v_d' = v_d/n_{aq}$ and $R = 1 + \dfrac{MV_{aq} \times K_{d\_aq}}{n_{aq}}$

or $\quad v_d' = v_d/n_e$ and $R = 1 + \dfrac{MV_{aq} \times K_{d\_aq}}{n_e}$

Symbol	Parameters	Dimensions	Units	Status
C_{e_nap} (x, y, z, t)	Pollutant concentration in dissolved phase in groundwater at the point with coordinates x, y, z and at instant t	$M.L^{-3}$	$mg.m^{-3}$	C or E
$C_{e\_nap,0}$	Pollutant concentration in dissolved phase in groundwater at the initial instant at the source	$M.L^{-3}$	$mg.m^{-3}$	C or E
$D_{eff,x,}$	Effectively dispersion coefficient in direction x	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
$D_{eff,y}$	Effectively dispersion coefficient in direction y	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
$D_{eff,z}$	Effectively dispersion coefficient in direction z	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
R	Delay coefficient	-	-	C
x	Distance from the source	L	m	E
y	Distance relative to the centre of the source	L	m	E
z	Distance relative to the top of the saturated zone	L	m	E
Y_{source_aq}	Width of the pollutant source in the saturated zone	L	m	E
Z_{source_aq}	Depth of the pollutant source in the saturated zone	L	m	E
λ_{aq}	Degradation coefficient of pollutant in the aquifer	T^{-1}	s^{-1}	E
V_d'	Water velocity	$L.T^{-1}$	$m.s^{-1}$	C

This solution assumes a homogeneous and isotropic aquifer and flux field. It is not suitable to represent situations where the flux field may be disturbed by pumping systems, when vertical fluxes can be disturbed by transport, and more generally when hydrological conditions can change over the modelled domain.

Potential limits to the Domenico solution have been presented by Guyonnet et al. (2004), Srinivasan et al. (2007) and West et al. (2007). It is recognised that this solution can result in errors, under certain conditions, particularly for high values of the longitudinal dispersivity. But this error remains negligible for reasonably low longitudinal dispersivity values. Guyonnet et al. (2004) showed that the Domenico solution was valid when the Peclet number[9] was greater than or equal to 6. Working on the basis of the comparison made by West et al. (2007) between the exact solution and Domenico's solution, the US EPA (http://epa.gov/ada/csmos/domenico.html) recommends using the latter for Peclet numbers greater than or equal to 10 (for which advection predominates over dispersion).

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[9] The Peclet number is therefore defined as the product of the average water velocity ($m.s^{-1}$), multiplied by the longitudinal distance (m) from the source to an arbitrary observation point, divided by the longitudinal dispersion coefficient ($m^2.s^{-1}$).

1.4.1.4. OTHER AVAILABLE MODELS AND RECOMMENDED APPROACH FOR ESTIMATING TRANSPORT OF POLLUTANTS IN SATURATED MEDIA

Numerous models exist to handle transport of pollutants in groundwater: analytical models, semi-analytical models, numerical models.

Analytical models, simplified simulation tools, use a mathematical solution for flow and/or transport equations for all points in time and space (cf. Domenico, 1987). The domain studied is not discretised by meshing, flow is generally uni-directional and continuous, and the medium is considered homogeneous and isotropic. In contrast, for a numerical model, the domain studied is discretised in space and time and a numerical diagram is used to solve the flow and transport equation (finite differences, finite elements, finite volumes, etc.).

Nor do analytical models take account of interactions with other media or with the matrix. Thus the great majority of them consider direct injection of pollutant into the saturated zone.

Numerous tools have been developed by the US EPA and are available on line (on the site http://www.epa.gov/ada/csmos/models.html). The reader can also refer to the Alberta Environment document on comparative assessment of models available to represent the future outcome of pollutants in the soil and groundwater (Alberta Environnement, 2005).

The following tools can be cited as examples:

- ANALGWST-PATCHF (Wexley, 1992 a and b)
- ART3D (Clement, 2001; Quezada et al., 2003; Jones et al., 2006)
- AT123D (Yeh, 1993)
- BIO 1D (Srinivasan et al., 1988; Maraqa et al., 2007)
- BIOCHLOR (US EPA, 2002)
- BIOSCREEN (US EPA, 1996b)
- MISP (BRGM, 2001, 2008)
- NAS (Chapelle et al., 2003; Mendez et al., 2004; Passerini et al., 2004)

Thus, BIOCHLOR (Aziz et al., 2000) is an analytical model that can be used to simulate the development of a specific pollution, and particularly natural attenuation of dissolved pollutants (chloroethenes or chloroethanes only[10]). The software, programmed in Excel, is based on the Domenico (1987) analytical solution, as modified by Martin-Hayden et al. (1997). It simulates advection, dispersion, sorption and biodegradation by reducing dechlorination (anaerobic condition with sequential 1st order degradation). This tool is as part of simulations relating to porous aquifers, with relatively homogenous sand-gravel lithology, and only simulates phenomena in saturated zones.

As part of work relating to the choice between analytical and numerical tools, the BIOCHLOR and NAS models have been tested and results from BIOCHLOR were compared with those from numerical tools (cf. http://transpol.ineris.fr/). For the case examined, with the available input data, it appeared that the simplest tools were capable of simulating the situation as precisely as numerical tools. However this similarity in results can be explained

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[10] Families of Halogenated Volatile Organic Compounds (HVOC).

by the fact that the comparative study conducted with numerical tools was greatly simplified (in terms of flow, representation of the source, etc.).

For the representation of other transfer models, it is better to remember that the choice of model should ultimately be dictated by:

- the phenomena considered,

- the objectives of the model,

- the available tools and suitability of the tool considered to the situation studied.

More precisely, the INERIS (2008a) report, reference DRC-08-86031-00620A, describes the information to be taken into account to choose between an analytical model and a numerical model when studying pollutant transfer in soils and groundwater. In summary, a pragmatic and iterative approach is recommended, highlighting and justifying reservations related to the results presented. The favoured approach, where possible, consists of firstly choosing a simple model (analytical or numerical, but with a lot of simplifying 'conservative' assumptions), then complicating the model if necessary, depending on the available input data/information. But, if there are too many uncertainties, new investigations should be performed.

1.4.2. POLLUTANT INFLOW TO THE WATER TABLE FROM A 'SOIL' SOURCE

As a first approach, vertically to a polluted zone, we can estimate the groundwater concentration attributable to the source studied, using the following mass balance:

$$L_s \times l_s \times h_{aq} \times \frac{dC_{e\_nap,site}}{\partial t} = L_s \times l_s \times C_{es,0} \times R_{ech}$$
$$- \left[R_{ech} \times L_s \times l_s + \left(l_s \times h_{aq} \times K_e \times i \right) \right] \times C_{e\_nap,site}$$

Equation 1.4.27

Integrating this equation over time intervals (Δt) where the parameters are constant gives:

$$C_{e\_nap,site}(t) = \frac{C_{es,0} \times R_{ech}}{R_{ech} + h_{aq} \times \dfrac{K_e \times i}{L_s}} \times \left(1 - e^{-\left(\frac{R_{ech}}{h_{aq}} + \frac{K_e \times i}{L_s} \right) \times \Delta t} \right)$$

Equation 1.4.28

$$+ C_{e\_nap,site}(t - \Delta t) \times e^{-\left(\frac{R_{ech}}{h_{aq}} + \frac{K_e \times i}{L_s} \right) \times \Delta t}$$

and under **steady state conditions**, we get:

$$C_{e\_nap,site} = \frac{C_{es,0} \times R_{ech}}{R_{ech} + h_{aq} \times \dfrac{K_e \times i}{L_s}}$$

Equation 1.4.29

Symbol	Parameters	Dimensions	Units	Status
$C_{e\_nap,site}$	Pollutant concentration in dissolved phase in groundwater, adjacent to the soil source	$M.L^{-3}$	$mg.m^{-3}$	C or E
$C_{es,0}$	Pollutant concentration in the soil water attributable to the source at the bottom of the vadose zone	$M.L^{-3}$	$mg.m^{-3}$	C or E
L_s	Length of the polluted zone	L	m	E
h_{aq}	Height of the aquifer	L	m	E
i	Hydraulic gradient (cf. section 1.4.1.1.1)	-	-	C or E
K_e	Hydraulic conductivity	$L.T^{-1}$	$m.s^{-1}$	C or E
R_{ech}	Leaching flux (cf. equation 1.1.48)	$L.T^{-1}$	$m.s^{-1}$	E

(l_s: width of the polluted zone)

Comment: The groundwater concentration of pollutant in dissolved phase, calculated from mass balance 1.4.27, does not take account of any ubiquitous man-made pollutant inflow and the geochemical background concentration. This is the concentration attributable to the soil source studied, excluding background concentration. Depending on the approach selected, the total concentration in dissolved phase in groundwater is estimated by adding the background concentration (cf. section 4) to this concentration, if the sum of these two concentrations remains less than the solubility of the pollutant in water.

There are more sophisticated models to represent the inflow of dissolved polluteant to the groundwater (CHEMFLO, US EPA, 2003; VLEACH, US EPA, 2007; SESOIL, Bonazountas et al., 1984). Some models use the Richards equation (Delage et al.) to represent flow in the soil of the vadose zone. In this equation, adapted from the Darcy equation, hydraulic conductivity is no longer considered constant, but as varying with the water content θ.

Thus, according to Richards, we state:

$$\frac{\partial \theta}{\partial t} = div[-K_e(\theta) \times \frac{\delta h}{\delta x} \times \vec{grad}(\theta)] + \frac{\delta K_e(\theta)}{\delta z}$$

Equation 1.4.30

where θ: volume fraction occupied by the soil water,

h_e: hydraulic load in the soil.

The relationship $K_e(\theta)$ should therefore be determined experimentally, representing one of the main difficulties of modelling transfer in the vadose zone.

1.5. 'SURFACE WATER' ENVIRONMENT

There are potentially a great many phenomena involved in the contamination of surface water.

Thus, a river or lake may be contaminated from various sources:

- point sources such as industrial discharge or an upstream tributary,
- a variety of sources associated with erosion and runoff from land within the watershed, atmospheric deposition or due to inflow from groundwater.

Discharged pollutants are transported by convection, diffusion and dispersion.

Exchanges can take place with the atmosphere (volatilisation) and the sediment layer (deposits and re-suspension of particles, or diffusion). Chemical reactions between different contained substances may cause precipitation or dilution phenomena, depending on changing chemical conditions. Degradation phenomena can take place in the water column and in the sediment layer.

Furthermore, hydraulic system can vary over time (from the low water flow rate to the peak flow rate) and in space (changes in cross-section and flow rate).

Modelling all these phenomena is complex. Only very simple approaches for estimating the concentration of pollutants in surface waters will be presented in this chapter. These approaches require little data and correspond to a steady state 'surface water' environment. They do not consider variations in the flow rate and cross-section of the watercourse, possible presence of stagnant areas, time and distance required for pollutants to be uniformly diluted in the aquatic environment.

Other models exist for more realistic and discriminating approaches (eg. EXAMS, US EPA 2004b; TOXRIV, Trapp et al. 1997, CORMIX, Doneker et al. 2007). But INERIS has no experience from using these tools.

In the same way as for soil, air and ground water, the expressions developed below are provided for calculating the concentration of pollutants in water attributable to local contamination sources, without considering inflows from ubiquitous sources of man-made pollutants and the geochemical background concentration. To distinguish between attributable concentrations and total concentrations and to estimate total concentrations, refer to section 4.

1.5.1. CONTAMINATION FROM A POINT DISCHARGE

The equations presented below are for calculating the steady-state pollutant concentration in a watercourse, downstream of a point discharge, potentially taking account of the reduction in water concentration caused by degradation, volatilisation and sedimentation phenomena. Diffusion between surface water and sediments is not considered (cf. limitations of the approach, section 1.5.1.4).

1.5.1.1. CALCULATING THE WATER CONCENTRATION AT THE OUTFALL

At the outfall, the pollutant concentration is calculated by assuming the **pollutant mixes instantaneously in the water**, hence:

$$C_{e\_sup}(x=0) = \frac{C_{rej} \times Q_{rej}}{Q^e_{e\_sup} + Q_{rej}}$$

Equation 1.5.1

Symbol	Parameters	Dimensions	Units	Status
$C_{e\_sup}(x=0)$	Pollutant concentration in surface water at the outfall	$M.L^{-3}$	$mg.m^{-3}$	C or E
C_{rej}	Pollutant concentration in the discharge	$M.L^{-3}$	$mg.m^{-3}$	E
Q_{rej}	Discharge flow rate	$L^3.T^{-1}$	$m^3.s^{-1}$	E
$Q^e_{e\_sup}$	Hydraulic flow rate in the watercourse upstream of the discharge	$L^3.T^{-1}$	$m^3.s^{-1}$	E

Comments:

1. The pollutant is not generally spread uniformly throughout the cross-section of the watercourse at the outfall (x=0). The distance required for the discharge to be completely diluted (so-called 'mixing distance') can actually be several kilometres. A short distance downstream of the outfall, the pollutant concentration may therefore be locally greater (in the imperfectly mixed flow from the discharge) than calculated using equation 1.5.1.

2. For another local pollution source upstream of this outfall, an additional term representing the contaminant concentration upstream of this point (excluding concentration due to the geochemical background concentration and ubiquitous man-made pollution) may be added to equation 1.5.1.

1.5.1.2. CALCULATING THE WATER CONCENTRATION DOWNSTREAM OF THE OUTFALL

The mass balance equation for the pollutant over a segment Δx of a watercourse is expressed as:

$$\frac{\Delta m_{e\_sup}}{\Delta t} = Q_{e\_sup}(x_{i-1}) \times C_{e\_sup}(x_{i-1}) - Q_{e\_sup}(x_i) \times C_{e\_sup}(x_i) - Vol_{e\_sup} \times \lambda_{e\_sup} \times C_{e\_sup}(x_i)$$

Equation 1.5.2

where m_{e_sup}: pollutant mass in water volume Vol_{e_sup},

C_{e_sup}: pollutant concentration in water volume Vol_{e_sup},

Q_{e_sup}: flow rate of the watercourse,

λ_{e_sup}: overall pollutant elimination coefficient (sum of elimination coefficients associated with degradation, volatilisation and sedimentation).

If the **flow rate** and **cross-section of the watercourse are constant** over segment Δx,

$$\frac{\Delta C_{e\_sup}}{\Delta t} = -v_{e\_sup} \times \frac{C_{e\_sup}(x_i) - C_{e\_sup}(x_{i-1})}{x_i - x_{i-1}} - \lambda_{e\_sup} \times C_{e\_sup}(x_i)$$

Equation 1.5.3

where v_{e_sup}: average water velocity,

$$v_{e\_sup} = \frac{Q_{e\_sup}}{S_{e\_sup}}$$

Equation 1.5.4

and S_{e_sup}: cross-section of the watercourse.

Writing equation 1.5.3 in differential form:

$$\frac{dC_{e\_sup}}{dt} = -v_{e\_sup} \times \frac{\partial C_{e\_sup}}{\partial x} - \lambda_{e\_sup} \times C_{e\_sup}$$ <div align="right">Equation 1.5.5</div>

At steady state,

$$\frac{\partial C_{e\_sup}(x)}{\partial x} = -\frac{\lambda_{e\_sup}(x)}{v_{e\_sup}} \times C_{e\_sup}(x)$$ <div align="right">Equation 1.5.6</div>

If λ_e and v_{e_sup} are constant in the direction of flow, integrating equation 1.5.6 yields:

$$C_{e\_sup}(x) = C_{e\_sup}(x=0) \times e^{(-\lambda_{e\_sup} \times \frac{x}{v_{e\_sup}})}$$ <div align="right">Equation 1.5.7</div>

or $\quad C_{e\_sup}(x) = \dfrac{C_{rej} \times Q_{rej}}{Q^e_{e\_sup} + Q_{rej}} \times e^{(-\lambda_{e\_sup} \times \frac{x}{v_{e\_sup}})}$ <div align="right">Equation 1.5.8</div>

Symbol	Parameters	Dimensions	Units	Status
C_{e_sup} (x)	Pollutant concentration in surface water at point x	M.L^{-3}	mg.m^{-3}	C or E
C_{rej}	Pollutant concentration in the discharge	M.L^{-3}	mg.m^{-3}	E
Q_{rej}	Discharge flow rate	L^3.T^{-1}	m^3.s^{-1}	E
$Q^e_{e\_sup}$	Hydraulic flow rate in the watercourse upstream of the discharge	L^3.T^{-1}	m^3.s^{-1}	E
λ_{e_sup}	Overall pollutant elimination coefficient (sum of elimination coefficients associated with degradation, volatilisation and sedimentation)	T^{-1}	s^{-1}	C or E
v_{e_sup}	Average water velocity	L.T^{-1}	m.s^{-1}	C or E

<u>Comments</u>:

1. For pollution upstream of the outfall (excluding concentration due to the geochemical background concentration and ubiquitous man-made pollution), we can state:

$$C_{e\_sup}(x) = \left(\frac{C_{rej} \times Q_{rej} + C^e_{e\_sup} \times Q^e_{e\_sup}}{Q^e_{e\_sup} + Q_{rej}} \right) \times e^{(-\lambda_{e\_sup} \times \frac{x}{v_{e\_sup}})}$$ <div align="right">Equation 1.5.9</div>

where $C^e_{e\_sup}$: pollutant concentration in the water upstream of the outfall.

2. Given the first comment in the previous section, equations 1.5.8 and 1.5.9 are valid if the outfall can be considered as perfectly mixed, i.e. from the so-called 'mixing distance'.

1.5.1.3. ESTIMATING THE ELIMINATION COEFFICIENT

Elimination phenomena may be considered or disregarded when estimating pollutant concentrations in surface water. Disregarding them results in overestimated pollutant concentrations. For a point discharge using the model developed above, disregarding elimination phenomena leads to a constant pollutant concentration downstream of the outfall along the entire length of the

watercourse. Conversely, considering elimination phenomena can result in water concentrations being underestimated.

The above elimination coefficient can include degradation, sedimentation and volatilisation phenomena:

$$\lambda_{e\_sup} = \lambda_d + \lambda_s + \lambda_v \qquad\qquad \text{Equation 1.5.10}$$

Symbol	Parameters	Dimensions	Units	Status
λ_{e_sup}	Overall pollutant elimination coefficient (sum of elimination coefficients associated with degradation, volatilisation and sedimentation) in surface water	T^{-1}	s^{-1}	C or E
λ_d	Degradation coefficient	T^{-1}	s^{-1}	C or E
λ_s	Sedimentation coefficient	T^{-1}	s^{-1}	C or E
λ_v	Volatilisation coefficient	T^{-1}	s^{-1}	C or E

Degradation mechanisms in water are hydrolysis (the hydrolysis mechanism is pH-dependent, so the hydrolysis constant can vary by several orders of magnitude, based on the pH value), photolysis and biodegradation. The mechanisms are represented by a first-order or pseudo first-order reaction, using an overall coefficient λ_d.

1.5.1.3.1. CALCULATING THE SEDIMENTATION COEFFICIENT

If there is no non-aqueous, liquid-phase pollutant denser than water, the pollutant mass sedimenting per unit time $\left\lfloor FM_{e\_sup} \right\rfloor_{sed}$ can be expressed as a function of the rate at which the depth of the sediment layer increases.

$$\left\lfloor FM_{e\_sup} \right\rfloor_{sed} = Vol_{e\_sup} \times \lambda_s \times C_{e\_sup} \qquad\qquad \text{Equation 1.5.11}$$

and $\quad \left\lfloor FM_{e\_sup} \right\rfloor_{sed} = A_{e\_sup} \times v_{sed} \times (1 - \theta_{sed}) \times MV_{p\_sed} \times C_{p\_e\_sup} \qquad$ Equation 1.5.12

hence $\quad \lambda_s = \dfrac{v_{sed}}{h_{e\_sup}} \times (1 - \theta_{sed}) \times MV_{p\_sed} \times \dfrac{C_{p\_e\_sup}}{C_{e\_sup}} \qquad$ Equation 1.5.13

where λ_s: sedimentation coefficient (or net particle deposition on the bed of the watercourse),

Vol_{e_sup}: volume of water considered,

A_{e_sup}: surface area of the body of water considered,

v_{sed}: rate at which the depth of the sediment layer increases,

h_{e_sup}: depth of the watercourse,

θ_{sed}: porosity of the sediment layer,

MV_{p_sed}: density of sediment particles,

$C_{p\_e\_sup}$: pollutant concentration on particles suspended in the water,

C_{e_sup}: concentration of dissolved and particulate pollutant in the surface water.

Thus, in the absence of pure-phase or water-immiscible pollutant,

$$C_{e\_sup} = C_{p\_e\_sup} \times MES + C_{d\_e\_sup} \qquad\qquad \text{Equation 1.5.14}$$

If the pollutant is in equilibrium between the particulate and dissolved phases and if the relationship between the concentration of pollutant adsorbed to suspended particles and the concentration dissolved in the water is given by:

$$K_{d\_MES} = \frac{C_{p\_e\_sup}}{C_{d\_e\_sup}}$$

Equation 1.5.15

where $C_{d\_e\_sup}$: dissolved pollutant concentration in surface water,

K_{d_MES} : pollutant partition coefficient between suspended matter and water,

MES: concentration of suspended particles in water,

then $\lambda_s = \dfrac{v_{sed}}{h_{e\_sup}} \times (1 - \theta_{sed}) \times MV_{p\_sed} \times \dfrac{K_{d\_MES}}{1 + K_{d\_MES} \times MES}$

Equation 1.5.16

Symbol	Parameters	Dimensions	Units	Status
λ_s	Sedimentation coefficient (or net particle deposition on the bed of the watercourse)	T^{-1}	s^{-1}	C or E
v_{sed}	Rate at which the depth of the sediment layer increases	L.T^{-1}	m.s^{-1}	E
h_{e_sup}	Depth of the watercourse	L	m	E
θ_{sed}	Porosity of the sediment layer	-	-	E
K_{d_MES}	Pollutant partition coefficient between suspended matter and water	L^3.M^{-1}	m^3.kg^{-1}	C or E
MV_{p_sed}	Density of sediment particles	M.L^{-3}	kg.m^{-3}	E
MES	Concentration of suspended particles in water	M.L^{-3}	kg.m^{-3}	E

λ_s can also be expressed as a function of the net deposition rate for suspended particles (resulting from exchanges between deposited and re-suspended particles). In fact, the increase in particulate mass in the sediment layer equals the mass of particles deposited. We can therefore state:

$$v_{sed} \times (1 - \theta_{sed}) \times MV_{p\_sed} = v_{MES} \times MES$$

Equation 1.5.17

where v_{MES}: net particle deposition rate,

hence $\lambda_s = \dfrac{v_{MES}}{h_{e\_sup}} \times MES \times \dfrac{K_{d\_MES}}{1 + K_{d\_MES} \times MES}$

Equation 1.5.18

Symbol	Parameters	Dimensions	Units	Status
λ_s	Sedimentation coefficient (or net particle deposition on the bed of the watercourse)	T^{-1}	s^{-1}	C or E
v_{MES}	Particle deposition rate (or net particle deposition on the bed of the watercourse)	L.T^{-1}	m.s^{-1}	C or E
h_{e_sup}	Depth of the watercourse	L	m	E
K_{d_MES}	Pollutant partition coefficient between suspended matter and water	L^3.M^{-1}	m^3.kg^{-1}	C or E
MES	Concentration of suspended particles in water	M.L^{-3}	kg.m^{-3}	E

1.5.1.3.2. CALCULATING THE VOLATILISATION COEFFICIENT

The mass transfer flux from surface water to the air $\lfloor FM_{e\_sup} \rfloor_{vol}$ is calculated from the mass transfer coefficient (K_v):

$$\lfloor FM_{e\_sup} \rfloor_{vol} = A_{e\_sup} \times K_v \times C_{d\_e\_sup}$$

Equation 1.5.19

and $\left\lfloor FM_{e\_sup} \right\rfloor_{vol} = Vol_{e\_sup} \times \lambda_v \times C_{e\_sup}$ Equation 1.5.20

hence $\lambda_v = \dfrac{K_v}{h_{e\_sup}} \times \dfrac{C_{d\_e\_sup}}{C_{e\_sup}}$ Equation 1.5.21

where Vol_{e_sup}: volume of water considered,

A_{e_sup}: surface area of the body of water considered,

h_{e_sup}: depth of the watercourse,

$C_{d\_e\_sup}$: pollutant concentration dissolved in the water,

C_{e_sup}: concentration of dissolved and particulate pollutant in the surface water.

According to equations 1.5.14 and 1.5.15, in the absence of pure-phase or water-immiscible pollutant, we can state:

$$\lambda_v = \frac{K_v}{h_{e\_sup} \times (1 + K_{d\_MES} \times MES)}$$ Equation 1.5.22

Symbol	Parameter	Dimensions	Units	Status
λ_v	Volatilisation coefficient	T^{-1}	s^{-1}	C or E
K_v	Mass transfer coefficient between surface water and air environments	$L.T^{-1}$	$m.s^{-1}$	C or E
h_{e_sup}	Depth of the watercourse	L	m	E
K_{d_MES}	Pollutant partition coefficient between suspended matter and water	$L^3.M^{-1}$	$m^3.kg^{-1}$	C or E
MES	Concentration of suspended particles in water	$M.L^{-3}$	$kg.m^{-3}$	E

Coefficient K_v is defined by assuming that pollutant transfer between the water and air compartments is determined by **diffusion across the two boundary layers separating these two compartments, themselves assumed to be perfectly mixed** (cf. diagram below). Each of these layers therefore presents a concentration gradient and the concentrations are discontinuous at the interface. K_v, which is the reciprocal of the sum of resistances for these two layers (in series), is equivalent to a conductance.

Air compartment

C_a

Air boundary layer C_a'

Water boundary layer C_e'

C_{e_sup}
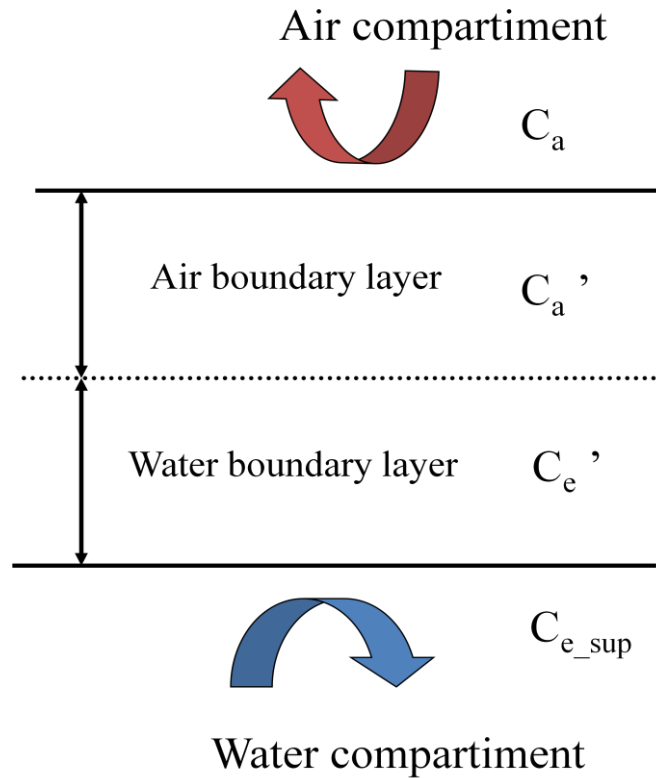
Water compartment

Figure 11: Model for transfer between the air and water compartments

Diffusion flux in the boundary layer of the water compartment is given by:

$$J_e = g_e \times (C_{d\_e\_sup} - C'_e)$$
<div align="right">Equation 1.5.23</div>

where g_e: conductance in the boundary layer of the water compartment or transfer coefficient in the liquid phase,

   C'_e: pollutant concentration in the boundary layer of the water environment.

Diffusion flux in the boundary layer of the air compartment is given by:

$$J_a = g_a \times (C'_{ag} - C_{ag,e})$$
<div align="right">Equation 1.5.24</div>

where g_e: conductance in the boundary layer of the air compartment or transfer coefficient in the gas phase,

   $C_{ag,e}$: gaseous pollutant concentration in the air compartment,

   C'_{ag}: gaseous pollutant concentration in the boundary of the air environment.

Concentrations C'_{ag} and C'_e are at equilibrium, hence we can state: $\dfrac{C'_{ag}}{C'_e} = H'$

where H': Henry constant (dimensionless).

According to the principle of conservation of mass, $J_a = J_e$

We can therefore state:

$$C'_e = \frac{g_e \times C_{d\_e\_sup} + g_a \times C_{ag,e}}{g_a \times H' + g_e}$$
<div align="right">Equation 1.5.25</div>

and $$J_e = J_a = g_e \times \left(C_{d\_e\_sup} - \frac{g_e \times C_{d\_e\_sup} + g_a \times C_{ag,e}}{g_a \times H' + g_e} \right)$$
<div align="right">Equation 1.5.26</div>

hence $J_e = J_a = \dfrac{g_e \times g_a \times H'}{g_a \times H' + g_e} \times \left(C_{d\_e\_\sup} - \dfrac{C_{ag,e}}{H'} \right)$ Equation 1.5.27

The mass transfer flux from surface water to the air [11] is expressed as:

$$\left[FM_{e\_\sup} \right]_{vol} = A_{e\_\sup} \times \dfrac{g_e \times g_a \times H'}{g_a \times H' + g_e} \times C_{d\_e\_\sup}$$ Equation 1.5.28

According to equations 1.5.19 and 1.5.28, we can therefore state:

$$K_v = \dfrac{g_e \times g_a \times H'}{g_a \times H' + g_e} = \left[\dfrac{1}{g_e} + \dfrac{1}{g_a \times H'} \right]^{-1}$$ Equation 1.5.29

Symbol	Parameters	Dimensions	Units	Status
K_v	Mass transfer coefficient between surface water and air compartments	$L.T^{-1}$	$m.s^{-1}$	C or E
g_e	Liquid phase transfer coefficient	$L.T^{-1}$	$m.s^{-1}$	C or E
g_a	Gas phase transfer coefficient	$L.T^{-1}$	$m.s^{-1}$	C or E
H'	Henry constant for the pollutant (dimensionless H' = H/[RxT])	-	-	C or E

Comments:

1. Different relationships exist to define g_e and g_a. They are often empirical relationships. These relationships depend on environmental conditions (depth of watercourse, flow rate, wind speed, etc.) and the physico-chemical properties of the chemicals (cf. Lyman 1990, Southworth 1979 and future documents about the physico-chemical properties of chemicals).

2. Lyman et al. (1990) made the following assessment of the volatilisation phenomenon from surface water based on the value of the Henry constant (H):

   - if H' < 4.10^{-6}, the chemical can be considered as non-volatile and water therefore evaporates more rapidly;

   - if 4.10^{-6} < H' < 4.10^{-4}, the chemical evaporates slowly and volatilisation is limited by diffusion in air. In shallow water, volatilisation can nonetheless be significant when H' is greater than 4.10^{-5};

   - if 4.10^{-4} < H' < 4.10^{-2}, volatilisation becomes significant and resistance in the gas and liquid phases is almost the same;

   - when H' > 4.10^{-2}, volatilisation is rapid and limited by the diffusion rate in water.

1.5.1.4. LIMITATIONS OF THE APPROACH DEVELOPED FOR A POINT DISCHARGE

The model presented above is used to calculate the pollutant concentration at steady state downstream of a discharge into a river or any other watercourse

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[11] The mass transfer flux from the air compartment to the surface water compartment is expressed as: $A_{e\_\sup} \times \dfrac{g_e \times g_a}{g_a \times H' + g_e} \times C_{ag,e}$. As this section disregards diffusional inflow from the atmosphere, this term is zero.

where the uni-dimensional assumption can be made. This model is not suitable for representing pollutant transport in estuaries and expanses of water with little current, such as lakes.

The model is based on the following assumptions:

- discharged pollutant flow, pollutant elimination coefficient (λ_e) and average speed of the water (v_{e_sup}), constant over sufficiently long periods that the pollutant concentration in the water reaches a steady state. Sporadic events such as floods cannot be taken into account;

- average speed of the water and pollutant elimination coefficient, constant in the direction of flow;

- instantaneous mixing of the pollutant with the watercourse: dispersion of the pollutant plume in the water is not considered;

- pollutant equilibrium reached between the adsorbed phase and the dissolved phase;

- diffusion between the sediment layer and water not considered. In this model, where the concentration in surface water is assumed to be steady, the top of the sediment layer (superficial sediment layer) can be considered to be at equilibrium with the surface water environment, because suspended sediment particles and those at the top of the sediment layer, where diffusion takes place, are at the same concentration.

  If diffusion involves a greater sediment thickness than that deposited during the discharge period, it is nonetheless possible for diffusion to have taken place between the surface water and the surface sediment layer (diffusion occurs as long as the concentration in the sediments over the thickness of the layer involved is different from that of the suspended particles);

- positive or zero net sedimentation flux: sedimentation is greater than or equal to re-suspension of particles from the sediment layer. In fact, if v_{sed} or v_{MES} is negative (sediment particles re-suspended faster than particles are deposited, meaning that the bed of the watercourse is being eroded) and if there is pollutant inflow into the water from a diffuse or sporadic source, an equilibrium state cannot exist between the sediments and surface water. Diffusion will necessarily occur from the water to the sediments.

1.5.2. DIFFUSE CONTAMINATION FROM THE ATMOSPHERE AND THE SOIL

The equations presented below are for calculating the pollutant concentration in an expanse of water or section of a watercourse, for a diffuse pollutant inflow from the air and/or the soil, taking account of the quantity of pollutant coming out and any reduction in the concentration in the water due to degradation, volatilisation and sedimentation phenomena.

As before, these equations do not consider diffusion between the water column and the underlying sediment layer. Given the limitations of the approach (cf. section 1.5.2.3), the pollutant concentration in surface water is only estimated at steady state.

In contrast to the model presented in section 1.5.1, the pollutant concentration is taken to be uniform in the volume considered. This volume may correspond to a segment of the watercourse with uniform hydraulic regime and watershed characteristics. The entire watercourse can therefore be represented by a

series of sequential segments, for each of which we can state a mass balance for the pollutant, as shown below:

$$\frac{dm_{e\_\sup}}{dt} = A_p + Q_{e\_\sup}^e \times C_{e\_\sup}^e - Q_{e\_\sup}^s \times C_{e\_\sup} - Vol_{e\_\sup} \times \lambda_{e\_\sup} \times C_{e\_\sup}$$ Equation 1.5.30

where m_{e_sup}: mass of pollutant in the water,

Vol_{e_sup}: volume of the expanse of water or section studied,

A_p: pollutant inflow to volume Vol_{e_sup},

C_{e_sup}: pollutant concentration in the water volume Vol_{e_sup},

$C_{e\_\sup}^e$: pollutant concentration upstream of volume Vol_{e_sup} (associated with a local pollution source, excluding concentration associated with geochemical background concentration or ubiquitous man-made pollution),

λ_{e_sup}: pollutant elimination constant (sum of elimination coefficients associated with degradation, volatilisation and sedimentation),

$Q_{e\_\sup}^s$ outgoing water flux,

$Q_{e\_\sup}^e$ incoming water flux.

hence $$\frac{dC_{e\_\sup}}{dt} = \frac{A_p + Q_{e\_\sup}^e \times C_{e\_\sup}^e}{Vol_{e\_\sup}} - \left(\frac{Q_{e\_\sup}^s}{Vol_{e\_\sup}} + \lambda_{e\_\sup} \right) \times C_{e\_\sup}$$ Equation 1.5.31

The outgoing water flux $Q_{e\_\sup}^s$ equals the sum of incoming flux into volume Vol_{e_sup} considered less the flux of evaporated water. **If water evaporation is considered to be compensated by precipitation onto the surface of the body of water**, then:

$$Q_{e\_\sup}^s \approx Q_{e\_\sup}^e + RO \times A_{bv}$$ Equation 1.5.32

where

RO: runoff,

A_{bv}: surface area of the watershed for the expanse of water or section of the watercourse considered.

Integrating this equation over time intervals where A_p, $Q_{e\_\sup}^e$, $Vol_{e\_\sup}$, $C_{e\_\sup}^e$, RO and λ_{e_sup} are constant, gives:

$$C_{e\_\sup}(t) = \frac{A_p + Q_{e\_\sup}^e \times C_{e\_\sup}^e}{Q_{e\_\sup}^s + Vol_{e\_\sup} \times \lambda_{e\_\sup}} \times \left(1 - \exp\left(\left(-\frac{Q_{e\_\sup}^s}{Vol_{e\_\sup}} - \lambda_{e\_\sup} \right) \times \Delta t \right) \right)$$ Equation 1.5.33

$$+ C_{e\_\sup}(t - \Delta t) \times \exp\left(\left(-\frac{Q_{e\_\sup}^s}{Vol_{e\_\sup}} - \lambda_{e\_\sup} \right) \times \Delta t \right)$$

When steady state is reached,

$$C_{e\_sup} = \frac{A_p + Q^e_{e\_sup} \times C^e_{e\_sup}}{Q^s_{e\_sup} + Vol_{e\_sup} \times \lambda_{e\_sup}}$$

Equation 1.5.34

Symbol	Parameters	Dimensions	Units	Status
C_{e_sup}	Pollutant concentration in the surface water	M.L^{-3}	mg.m^{-3}	C or E
A_p	Pollutant inflow to the expanse of water or section of the watercourse considered	M.T^{-1}	mg. s^{-1}	C or E
Vol_{e_sup}	Volume of the body of water considered	L^3	m^3	E
$Q^e_{e\_sup}$	Incoming flow rate	L^3.T^{-1}	m^3.s^{-1}	E
$Q^s_{e\_sup}$	Outgoing flow rate	L^3.T^{-1}	m^3.s^{-1}	C or E
$C^e_{e\_sup}$	Upstream pollutant concentration (associated with a local source, excluding concentration associated with geochemical background concentration or ubiquitous man-made pollution)	M.L^{-3}	mg.m^{-3}	E
λ_{e_sup}	Pollutant elimination coefficient (sum of elimination coefficients associated with degradation, volatilisation and sedimentation) in surface water	T^{-1}	s^{-1}	C or E
RO	Runoff	L.T^{-1}	m.s^{-1}	E
A_{bv}	Surface area of watershed for the expanse of water or section of the watercourse considered	L^2	m^2	E

1.5.2.1. INFLOWS FROM THE ATMOSPHERE AND SOIL

1.5.2.1.1. INFLOWS FROM THE ATMOSPHERE

This is direct deposition of pollutant as particles and gases onto the surface of the water volume considered.

$$A_a = \left(D_{pe} + D_{ge}\right) \times A_{e\_sup}$$

Equation 1.5.35

where A_a : pollutant inflow to the expanse of water or section of the watercourse considered from the atmosphere,

A_{e_sup}: surface area of the water volume considered,

D_{pe}: particle deposition on the water volume considered,

D_{pe}: gas deposition on the water volume considered.

As indicated in section 1.1.2.2.1, particle deposition may comprise a dry flux and a wet flux (particles leached by precipitation).

$$D_{pe} = D_{pse} + D_{phe}$$

Equation 1.5.36

Similarly, gas deposition may comprise a dry flux (diffusion) and a wet flux (leaching and dissolution of gases in water).

$$D_{ge} = D_{gse} + D_{ghe}$$

Equation 1.5.37

Symbol	Parameters	Dimensions	Units	Status
A_a	Pollutant inflow to the expanse of water or section of the watercourse considered from the atmosphere	$M.T^{-1}$	$mg.s^{-1}$	C or E
A_{e_sup}	Surface area of the water volume considered	L^2	m^2	E
D_{pe}	Pollutant flux as particles onto the water volume considered	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
D_{pse}	Dry particle pollutant flux onto the water volume considered	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
D_{phe}	Wet particle pollutant flux onto the water volume considered	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
D_{ge}	Pollutant flux as gas onto the water volume considered	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
D_{gse}	Dry gas pollutant flux onto the water volume considered	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
D_{ghe}	Wet gas pollutant flux onto the water volume considered	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E

As indicated in section 1.1.2.2.1 for soil deposition, dispersion models generally enable the various depositions described above to be estimated. But there are also simplified methods for estimating this deposition.

Comments:

1. The expression used to model dry deposition (as opposed to wet deposition) depends on the surface where deposition occurs. Dry deposition is expressed from the pollutant concentration in the air and rate of deposition, which depends on the roughness of the study area and the nature of the deposition surface (for dry gas deposition). Consequently, for the same concentration in air, dry particle and gas deposition onto soil (D_{pss} and D_{gss}) are different from dry particle and gas deposition onto an expanse of water (D_{pse} and D_{gse}).

2. Dry gas deposition can also be interpreted as the transfer flux by diffusion from the atmosphere into the water environment. This flux can therefore be estimated using the model for boundary layers between two environments, developed in section 1.5.1.3.2. According to this model, we can state:

$$D_{gse} = K_v \times \frac{F_g \times C_a}{H'}$$

Equation 1.5.38

Symbol	Parameters	Dimensions	Units	Status
D_{gse}	Dry gas pollutant flux onto the water volume considered	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
K_v	Mass transfer coefficient	$L.T^{-1}$	$m.s^{-1}$	E
H'	Henry constant (dimensionless): H' = H/RT	-	-	C or E
C_a	Pollutant concentration in the air	$M.L^{-3}$	$mg.m^{-3}$	C or E
F_g	Pollutant fraction in gaseous form	-	-	C or E

1.5.2.1.2. INFLOWS FROM THE SOIL

Inflows from the soil can be due to erosion and runoff.

1.5.2.1.2.1. INFLOW BY EROSION

The inflow by erosion is:

$$A_e = X_{e\_bv\_sc\_ni} \times SD_{sc} \times ER \times (A_{bv\_sc} - A_{bvi\_sc}) \times C_s$$

Equation 1.5.39

where C_s: pollutant concentration in the soil,

$X_{e\_bv\_sc\_ni}$: mass of soil detached and transported by erosion, per unit surface area and per unit time, from the contaminated, permeable surface of the watershed,

SD_{sc} : ratio between the mass of material transported downstream and the mass eroded from the contaminated, permeable surface of the watershed,

A_{bv_sc}: surface area of watershed for the expanse of water or section of the watercourse considered, in which the soil is contaminated by the source studied,

A_{bvi_sc}: impermeable surface area of watershed for the expanse of water or section of the watercourse considered, in which the soil is contaminated by the source studied,

ER: enrichment ratio.

As indicated in section 1.1.2.3.3.2, an enrichment ratio can be introduced to take account of the fact that eroded particles have often higher concentrations than the soil *in situ*.

$X_{e\_bv\_sc\_ni}$ can be estimated from the Universal Soil Loss Equation (cf. section 1.1.2.3.3.1).

SD_{sc} can be estimated from the empirical relationship defined by Vanoni (1975) and reproduced in US EPA documents (1998, 2005):

$$SD_{sc} = a * (A_{bv\_sc})^{-b}$$

Equation 1.5.40

where *a* is defined using the surface area of the zone considered, as indicated below:

surface area of the study zone (m²)	a
$A_{bv\_sc} \leq 2.59 \times 10^5$	2.1
$2.59 \times 10^5 < A_{bv\_sc} \leq 2.59 \times 10^6$	1.9
$2.59 \times 10^6 < A_{bv\_sc} \leq 2.59 \times 10^7$	1.4
$2.59 \times 10^7 < A_{bv\_sc} \leq 2.59 \times 10^8$	1.2
$2.59 \times 10^8 < A_{bv\_sc}$	0.6

and b = 0.125.

Estimates for $X_{e\_bv\_sc\_ni}$ and SD_{sc} must be based on the characteristics of the watershed zone, where the soil is contaminated by the source; the watershed to be defined is the expanse of water or section of the watercourse considered.

Symbol	Parameters	Dimensions	Units	Status
A_e	Pollutant inflow to the expanse of water or section of the watercourse studied per unit time due to water erosion	$M.T^{-1}$	$mg.s^{-1}$	C or E
$X_{e\_bv\_sc\_ni}$	Mass of soil detached and transported by erosion, per unit surface area and per unit time, from the contaminated, permeable surface of the watershed	$M.L^{-2}.T^{-1}$	$kg.m^{-2}.s^{-1}$	C or E
SD_{sc}	Ratio between the mass of material transported downstream and the mass eroded from the contaminated, permeable surface of the watershed	-	-	C or E
ER	Enrichment ratio (cf. section 1.1.2.3.3.2)	-	-	E
A_{bv_sc}	Surface area of watershed for the expanse of water or section of the watercourse considered, in which the soil is contaminated by the source studied	L^2	m^2	E
A_{bvi_sc}	Permeable surface area of watershed for the expanse of water or section of the watercourse considered, in which the soil is contaminated by the source studied	L^2	m^2	E
C_s	Pollutant concentration in the soil of the zone considered	$M.M^{-1}$	$mg.kg^{-1}$	C or E

Comment: the US EPA (1998, 2005) uses the pollutant concentration adsorbed to soil particles instead of the concentration C_s in equation 1.5.39 (see discussion relating to this point in section 1.1.2.3.3.2).

1.5.2.1.2.2. INFLOW BY RUNOFF

For runoff inflow, there is a distinction between impermeable and permeable zones of the watershed.

1. Pollutants deposited by the atmosphere on the impermeable zones can run into expanses of water or rivers when it rains.

   If it is assumed that all atmospheric depositions onto the impermeable zones of the section of watershed located upstream of the expanse of water or the section of watercourse considered are combined with this water volume (conservative assumption used by the US EPA (1998, 2005)), then:

$$A_{ri} = \left(D_{ps} + D_{gs}\right) \times A_{bvi\_sc}$$
<div align="right">Equation 1.5.41</div>

Symbol	Parameters	Dimensions	Units	Status
A_{ri}	Pollutant inflow to the expanse of water or section of the watercourse considered by runoff from the impermeable areas of the watershed	$M.T^{-1}$	$mg.s^{-1}$	C or E
D_{ps}	Particulate pollutant flux over the impermeable area of watershed for the expanse of water or section of the watercourse considered	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
D_{gs}	Gaseous pollutant influx over the impermeable area of watershed for the expanse of water or section of the watercourse considered	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
A_{bvi_sc}	Permeable surface area of watershed for the expanse of water or section of the watercourse considered, in which the soil is contaminated by direct deposition from the atmosphere	L^2	m^2	E

Ref: DRC-14-141968-04378A

2. For impermeable, contaminated areas located upstream of the expanse of water or section of the watercourse considered, the US EPA estimates the inflow by runoff as follows:

$$A_r = RO \times (A_{bv\_sc} - A_{bvi\_sc}) \times C_{es}$$

Equation 1.5.42

According to equation 1.1.11, **if the pollutant concentration in the soil porewater is less than solubility** and **if multiphase equilibrium is reached in the soil**:

$$A_r \approx RO \times (A_{bv\_sc} - A_{bvi\_sc}) \times \frac{MV_s}{MV_s \times K_d + \theta} \times C_s$$

Equation 1.5.43

(cf. section 1.1.2.3.2)

But **equations 1.5.42 and 1.5.43 assume that**:

- **the pollutant concentration in the soil layer is uniform,**
- **all the water running off the soil is at equilibrium with the soil contamination**. For reasons of kinetics, this assumption tends to overestimate the pollutant inflow from runoff significantly. INERIS only considers this inflow by runoff over impermeable surfaces in an approach intended to deliberately overestimate surface water contamination.

Symbol	Parameters	Dimensions	Units	Status
A_r	Pollutant inflow to the expanse of water or section of the watercourse considered by runoff from the permeable areas of the watershed	$M.T^{-1}$	$mg.s^{-1}$	C or E
A_{bv_sc}	Surface area of watershed for the expanse of water or section of the watercourse considered, in which the soil is contaminated by the source studied	L^2	m^2	E
A_{bvi_sc}	Permeable surface area of watershed for the expanse of water or section of the watercourse considered, in which the soil is contaminated by the source studied	L^2	m^2	E
RO	Runoff	$L.T^{-1}$	$m.s^{-1}$	E
C_s	Pollutant concentration in the soil	$M.M^{-1}$	$mg.kg^{-1}$	C or E
θ	Volume fraction occupied by soil water	-	-	E
K_d	Partition coefficient between soil particles and soil water	$L^3.M^{-1}$	$m^3.kg^{-1}$	C or E
MV_s	Bulk soil density	$M.L^{-3}$	$kg.m^{-3}$	E

1.5.2.2. ESTIMATING THE ELIMINATION COEFFICIENT

As indicated in section 1.5.1.3, elimination phenomena may be considered or disregarded when estimating pollutant concentrations in surface water. Disregarding them results in overestimating pollutant concentrations. Conversely, taken them into account can result in underestimating concentrations.

The elimination coefficient (λ_{e_sup}) has been defined in section 1.5.1.3. It includes degradation, sedimentation and volatilisation phenomena.

$$\lambda_{e\_sup} = \lambda_d + \lambda_s + \lambda_v$$

<div align="right">Equation 1.5.44</div>

The expression for the volatilisation coefficient (λ_v) has been given in section 1.5.1.3.2.

The sedimentation coefficient (λ_s) has been defined in section 1.5.1.3.1. Two expressions has been proposed for this parameter. One depends on the net deposition rate for suspended particles:

$$\lambda_s = \frac{v_{MES}}{h_{e\_sup}} \times MES \times \frac{K_{d\_MES}}{1 + K_{d\_MES} \times MES}$$

<div align="right">Equation 1.5.45</div>

However, **if the suspended matter content in the water is constant in time and space, and if the quantities of particles entering from the atmosphere and by runoff over impermeable areas are negligible compared to inflows from erosion**, then:

$$v_{MES} = \frac{X_{e\_bv\_ni} \times (A_{bv} - A_{bvi}) \times SD + (Q^e_{e-sup} - Q^s_{e\_sup}) \times MES}{A_{e-sup} \times MES}$$

<div align="right">Equation 1.5.46</div>

hence $$\lambda_s = \frac{X_{e\_bv\_ni} \times (A_{bv} - A_{bvi}) \times SD + (Q^e_{e-sup} - Q^s_{e\_sup}) \times MES}{A_{e-sup} \times h_{e\_sup}} \times \frac{K_{d\_MES}}{1 + K_{d\_MES} \times MES}$$

<div align="right">Equation 1.5.47</div>

The product $X_{e\_bv\_ni} \times (A_{bv} - A_{bvi}) \times SD$ represents the quantity of soil particles flowing into the expanse of water or section of the watercourse considered due to water erosion, whether or not these particles are contaminated. $(A_{bv} - A_{bvi})$ represents the permeable area of the watershed for the expanse of water or section of the watercourse considered (whether or not this area is contaminated).

$X_{e\_bv\_ni}$ can be estimated using the Universal Soil Loss Equation (cf. section 1.1.2.3.3.1). SD can be estimated using the approach presented in section 1.5.2.1.2.1, replacing the surface area of the contaminated watershed (A_{bv_sc}) by the surface area of the watershed (A_{bv}) for the expanse of water or section of the watercourse considered.

Symbol	Parameters	Dimensions	Units	Status
λ_s	Sedimentation coefficient (corresponding to the net particle deposition on the bed of the watercourse)	T^{-1}	s^{-1}	C or E
v_{MES}	Particle deposition rate (corresponding to the net particle deposition on the bed of the watercourse)	$L.T^{-1}$	$m.s^{-1}$	C or E
A_{bv}	Surface area of watershed for the expanse of water or section of the watercourse considered	L^2	m^2	E
A_{bvi}	Impermeable surface area of watershed for the expanse of water or section of the watercourse considered	L^2	m^2	E
$X_{e\_bv\_ni}$	Mass of soil detached and transported by erosion from the permeable surface of the watershed, per unit surface area and per unit time	$M.L^{-2}.T^{-1}$	$kg.m^{-2}.s^{-1}$	C or E
SD	Ratio between the mass of material transported downstream and the mass eroded	-	-	C or E
$Q^e_{e\_sup}$	Incoming flow rate	$L^3.T^{-1}$	$m^3.s^{-1}$	E
$Q^s_{e\_sup}$	Outgoing flow rate	$L^3.T^{-1}$	$m^3.s^{-1}$	C or E
h_{e_sup}	Depth of the expanse of water or section of the watercourse considered	L	m	E
K_{d_MES}	Pollutant partition coefficient between suspended particles and water	$L^3.M^{-1}$	$m^3.kg^{-1}$	C or E
MES	Concentration of suspended particles in water	$M.L^{-3}$	$kg.m^{-3}$	E

1.5.2.3. LIMITATIONS OF THE MODEL

The model presented above is used to calculate the steady-state pollutant concentration, in a volume of water assumed to be homogeneous or immediately downstream of this volume of water.

This model is dimensionless and too simplified to represent pollutant transport in estuaries.

It is based on the following assumptions:

- uniform pollutant concentration in the volume of water, which assumes uniform inflow and elimination of pollutant over the entire volume considered;
- pollutant equilibrium reached between the adsorbed phase and the dissolved phase;
- diffusion between the sediment layer and water is not considered. If the concentration in surface water remains constant over sufficiently long periods, the superficial sediment layer can be considered to be at equilibrium with the surface water environment, because suspended sediment particles and those at the top of the sediment layer, where diffusion takes place, are at the same concentration.

  For this reason, this model is only used to estimate the concentration in surface water (C_{e_sup}) at steady state using equation 1.5.34. The parameters A_p, $Q^e_{e\_sup}$, Vol_{e_sup}, $C^e_{e\_sup}$, RO and λ_{e_sup} must be constant over sufficiently long periods so that the concentration in the water reaches a

steady level. To do so, we can confirm that equation 1.5.33 (giving C_{e_sup} as a function of time) gives a very similar result to equation 1.5.34.

If pollutant inflows into the water vary with time and if diffusion involves a greater sediment thickness than that deposited during the constant inflow period considered, it is nonetheless possible for diffusion to have taken place between the surface water and the surface sediment layer (diffusion occurs as long as the concentration in the sediments over the thickness of the layer involved is different from that of the suspended particles). If the pollutant inflow increases over time, diffusion may occur from the surface water into the superficial sediment layer. Failing to take account of diffusion in the model will therefore tend to overestimate the concentration in surface water. Conversely, if the pollutant inflow falls over time, diffusion may occur from the sediments into the surface water and the concentration in surface water will tend to be underestimated;

- positive or zero net sedimentation flux: sedimentation is greater than or equal to re-suspension of particles from the sediment layer. In fact, if v_{sed} or v_{MES} is negative (sediment particles re-suspended faster than particles are deposited, meaning that the bed of the watercourse is being eroded) and if there is pollutant inflow into the water from a diffuse or sporadic source, an equilibrium state cannot exist between the sediments and surface water. Diffusion will necessarily occur from the water to the sediments.

Consequently, this model enables the average pollutant concentration in the water to be evaluated over the long term. It is not suitable for representing the situation of water being contaminated by pollutants leaching (re-suspended particles or solubilisation of adsorbed pollutants) from sediments accumulated during more significant pollution episodes of the water, for example.

1.5.3. APPROACH TO BE USED FOR A POINT DISCHARGE AND CONCOMITANT DIFFUSE CONTAMINATION

If the volume of water considered is both the site of point discharge and diffuse contamination, the resulting pollutant concentration in the water can be calculated using one or other of the approaches developed above (section 1.5.1 or section 1.5.2), depending on the conditions of the site studied and the objectives sought.

Based on the approach developed in section 1.5.1 (and taking the same assumptions into account: cf. section 1.5.1.4), considering a diffuse discharge along the watercourse in addition to a point discharge leads to:

$$\frac{dC_{e\_sup}}{dt} = -\frac{\partial(v_{e\_sup} \times C_{e\_sup})}{\partial x} - \lambda_{e\_sup} \times C_{e\_sup} + \frac{A'_p}{h_{e\_sup}} \qquad \text{Equation 1.5.48}$$

where A'_p: pollutant inflow into the watercourse per unit area,

h_{e_sup}: depth of the watercourse.

At steady state,

$$\frac{\partial(v_{e\_sup}(x) \times C_{e\_sup}(x))}{\partial x} = -\lambda_{e\_sup}(x) \times C_{e\_sup}(x) + \frac{A'_p}{h_{e\_sup}(x)} \qquad \text{Equation 1.5.49}$$

If λ_{e_sup}, v_{e_sup}, A'_p and h_{e_sup} are constant in the direction of flow (pollutant inflow over the portion of watercourse studied does not cause the rate of flow or depth of the watercourse to vary (negligible variations), the integrating equation 1.5.49 yields:

$$C_{e\_sup}(x) = C_{e\_sup}(x=0) \times e^{\left(-\lambda_{e\_sup} \times \frac{x}{v_{e\_sup}}\right)} + \frac{A'_p}{h_{e\_sup} \times \lambda_{e\_sup}} \times \left(1 - e^{\left(-\lambda_{e\_sup} \times \frac{x}{v_{e\_sup}}\right)}\right)$$ Equation 1.5.50

where $C_{e\_sup}(x=0) = \dfrac{C_{rej} \times Q_{rej}}{Q_{e\_sup} + Q_{rej}}$ for a point discharge with concentration C_{rej} and flow rate

Q_{rej} at point x=0

and $C_{e\_sup}(x=0) = \dfrac{C_{rej} \times Q_{rej} + C^e_{e\_sup} \times Q^e_{e\_sup}}{Q^e_{e\_sup} + Q_{rej}}$, if the watercourse also has a pollutant

concentration of $C^e_{e\_sup}$ upstream of the discharge.

Symbol	Parameter	Dimensions	Units	Status
C_{e_sup}	Pollutant concentration in the surface water	$M.L^{-3}$	mg.m^{-3}	C or E
A'_p	Pollutant inflow from the soil and atmosphere into the watercourse per unit area	$M.L^{-2}.T^{-1}$	m^{-2}.s^{-1}	C or E
v_{e_sup}	Average water velocity	$L.T^{-1}$	m.s^{-1}	C or E
$Q^e_{e\_sup}$	Hydraulic flow rate in the watercourse upstream of the discharge	$L^3.T^{-1}$	m^3.s^{-1}	E
Q_{rej}	Discharge flow rate	$L^3.T^{-1}$	m^3.s^{-1}	E
λ_{e_sup}	Pollutant elimination coefficient (sum of elimination coefficients associated with degradation, volatilisation and sedimentation)	T^{-1}	s^{-1}	C or E
C_{rej}	Pollutant concentration in the discharge	$M.L^{-3}$	mg.m^{-3}	E
$C^e_{e\_sup}$	Pollutant concentration in water upstream of the discharge (associated with a local source, excluding concentration associated with geochemical background concentration or ubiquitous man-made pollution)	$M.L^{-3}$	mg.m^{-3}	E
h_{e_sup}	Depth of the watercourse	L	m	E

If the dimensionless model developed in section 1.5.2 is used, the point discharge must be considered as homogenised in the body of water studied. The mass balance for the pollutant in the body of water gives:

$$\frac{dm_{e\_sup}}{dt} = A_p + Q^e_{e\_sup} \times C^e_{e\_sup} + Q_{rej} \times C_{rej}$$

$$- (Q^e_{e\_sup} + Q_{rej} + RO \times A_{bv}) \times C_{e\_sup} - Vol_{e\_sup} \times \lambda_{e\_sup} \times C_{e\_sup}$$

Equation 1.5.51

$$\frac{dC_{e\_sup}}{dt} = \frac{A_p + Q^e_{e\_sup} \times C^e_{e\_sup} + Q_{rej} \times C_{rej}}{Vol_{e\_sup}}$$

$$- \frac{(Q^e_{e\_sup} + Q_{rej} + RO \times A_{bv}) \times C_{e\_sup}}{Vol_{e\_sup}} - \lambda_{e\_sup} \times C_{e\_sup}$$

<div align="right">Equation 1.5.52</div>

Integrating in time intervals where A_p, $Q^e_{e\_sup}$, Vol_{e_sup}, $C^e_{e\_sup}$, RO, Q_{rej}, C_{rej} and λ_{e_sup} are constant:

$$C_{e\_sup}(t) = \frac{A_p + Q^e_{e\_sup} \times C^e_{e\_sup} + Q_{rej} \times C_{rej}}{Q^e_{e\_sup} + Q_{rej} + RO \times A_{bv} + Vol_{e\_sup} \times \lambda_e}$$

$$\times \left(1 - e^{-\left(\frac{Q^e_{e\_sup}+Q_{rej}+RO\times A_{bv}}{Vol_{e\_sup}}+\lambda_e\right)\times\Delta t} \right) + C_{e\_sup}(t-\Delta t) \times e^{-\left(\frac{Q^e_{e\_sup}+Q_{rej}+RO\times A_{bv}}{Vol_{e\_sup}}+\lambda_e\right)\times\Delta t}$$

<div align="right">Equation 1.5.53</div>

At steady state:

$$C_{e\_sup} = \frac{A_p + Q^e_{e\_sup} \times C^e_{e\_sup} + Q_{rej} \times C_{rej}}{Q^e_{e\_sup} + Q_{rej} + RO \times A_{bv} + Vol_{e\_sup} \times \lambda_e} \qquad \text{Equation 1.5.54}$$

The limitations described in section 1.5.2.3 apply to this equation (the discharged pollutant flux must also be constant over sufficiently long periods that the pollutant concentration in the water reaches a steady level). Concentration C_{e_sup} will only be estimated at steady state and it can be checked that equation 1.5.53 gives a very similar result to equation 1.5.54.

Symbol	Parameter	Dimensions	Units	Status
C_{e_sup}	Pollutant concentration in the surface water	M.L^{-3}	mg.m^{-3}	C or E
A_p	Pollutant inflow from the soil and atmosphere into the body of water	M	mg	C or E
Vol_{e_sup}	Volume of the body of water considered	L^3	m^3	E
λ_{e_sup}	Pollutant elimination coefficient (sum of elimination coefficients associated with degradation, volatilisation and sedimentation) in surface water	T^{-1}	s^{-1}	C or E
C_{rej}	Pollutant concentration in the discharge	M.L^{-3}	mg.m^{-3}	E
Q_{rej}	Discharge flow rate	L^3.T^{-1}	m^3.s^{-1}	E
$Q^e_{e\_sup}$	Incoming hydraulic flow rate	L^3.T^{-1}	m^3.s^{-1}	E
$Q^s_{e\_sup}$	Outgoing hydraulic flow rate	L^3.T^{-1}	m^3.s^{-1}	C or E
$C^e_{e\_sup}$	Pollutant concentration in water upstream of the discharge (associated with a local source, excluding concentration associated with geochemical background concentration or ubiquitous man-made pollution)	M.L^{-3}	mg.m^{-3}	E
RO	Runoff	L.T^{-1}	m.s^{-1}	E
A_{bv}	Surface area of watershed for the expanse of water or section of the watercourse considered	L^2	m^2	E

Comment: As previously indicated, the expressions developed in sections 1.5.1, 1.5.2 and 1.5.3 are provided for calculating the pollutant concentration in water attributable to the contamination sources studied, without considering ubiquitous man-made pollutant sources and the geochemical background concentration. The total concentration in surface water is therefore estimated by adding the background concentration in the water to this concentration (cf. section 4).

1.5.4. POLLUTANT CONCENTRATION DISSOLVED IN WATER

The pollutant concentration dissolved in the water may be needed to calculate exposure by ingesting the water and the pollutant concentration in aquatic organisms.

According to equations 1.5.14 and 1.5.15,

$$C_{d\_e\_sup} = \frac{C_{e\_sup}}{1 + K_{d\_mes} \times MES} \qquad \text{Equation 1.5.55}$$

Symbol	Parameter	Dimensions	Units	Status
$C_{d\_e\_sup}$	Pollutant concentration dissolved in surface water	$M.L^{-3}$	$mg.m^{-3}$	C or E
C_{e_sup}	Pollutant concentration in the surface water	$M.L^{-3}$	$mg.m^{-3}$	C or E
K_{d_MES}	Pollutant partition coefficient between suspended matter and water	$L^3.M^{-1}$	$m^3.kg^{-1}$	C or E
MES	Concentration of suspended particles in water	$M.L^{-3}$	$kg.m^{-3}$	E

1.5.5. CONCENTRATIONS IN THE SUPERFICIAL SEDIMENT LAYER

The concentration of certain substances in aquatic organisms can also be calculated from the pollutant concentration on particles in the sediment layer (as in US EPA 2005).

The pollutant is present in the sediment layer in dissolved phase and adsorbed onto particles:

$$m_{sed} = m_{p\_sed} + m_{d\_sed}$$

Equation 1.5.56

where m_{sed}: total mass of pollutant in the sediment layer,

m_{p_sed}: mass of pollutant adsorbed to sediment particles.

According to the expression of pollutant masses in each phase of the sediment layer, equation 1.5.56 can be written:

$$(1-\theta_{sed}) \times MV_{p\_sed} \times V_s \times C_{sed} = (1-\theta_{sed}) \times MV_{p\_sed} \times V_s \times C_{p\_sed} + C_{d\_sed} \times \theta_{sed} \times V_s$$

Equation 1.5.57

where C_{sed}: pollutant concentration in sediments in dissolved and particulate phases (expressed as dry weight),

C_{d_sed}: pollutant concentration in the water of the sediment layer,

C_{p_sed}: pollutant concentration on sediment particles,

MV_{p_sed}: density of sediment particles,

θ_{sed}: porosity of the sediment layer,

V_s: volume of the sediment layer considered.

If the pollutant is in equilibrium between the superficial sediment layer and the surface water environment and if there is an equilibrium between the dissolved and particulate phases of the superficial sediment layer, we can state:

$$C_{d\_sed} = C_{d\_e\_sup}$$

Equation 1.5.58

$$K_{d\_MES} = \frac{C_{p\_sed}}{C_{d\_sed}},$$

Equation 1.5.59

$$C_{sed} = C_{d\_e\_sup} \times \left(K_{d\_MES} + \frac{\theta_{sed}}{(1-\theta_{sed}) \times MV_{p\_sed}} \right)$$

Equation 1.5.60

and $$C_{p\_sed} = \frac{(1-\theta_{sed}) \times MV_{p\_sed} \times K_{d\_MES}}{(1-\theta_{sed}) \times MV_{p\_sed} \times K_{d\_MES} + \theta_{sed}} \times C_{sed}$$

Equation 1.5.61

Symbol	Parameter	Dimensions	Units	Status
C_{sed}	Pollutant concentration (dissolved and adsorbed phases) in the superficial sediment layer	$M.M^{-1}$	$mg.kg^{-1}$	C or E
C_{p_sed}	Pollutant concentration adsorbed on superficial sediment particles	$M.M^{-1}$	$mg.kg^{-1}$	C or E
θ_{sed}	Porosity of the superficial sediment layer	-	-	E
K_{d_MES}	Pollutant partition coefficient in the superficial sediment layer and between suspended particles and water	$L^3.M^{-1}$	$m^3.kg^{-1}$	C or E
MV_{p_sed}	Density of sediment particles	$M.L^{-3}$	$kg.m^{-3}$	E
$C_{d\_e\_sup}$	Pollutant concentration in dissolved phase in surface water	$M.L^{-3}$	$mg.m^{-3}$	C or E
C_{d_sed}	Dissolved concentration of pollutant in the water of the sediment layer	$M.L^{-3}$	$mg.m^{-3}$	C or E

1.6. PLANT PRODUCTS

Because certain pollutants accumulate in the food chain, assessing human exposure requires estimating concentrations in plant and animal products. They are estimated by measurement or modelling.

When evaluating the risks associated with a site, we are concerned with:

- the attributable risk associated with this site. This means taking account of exposures associated with locally-sourced products. Given the industrialisation of food products and the national (indeed international) nature of distribution networks, this really means home-grown foods produced by consumers that are generally considered when estimating the risk attributable to the site through food. However, if site-specific data indicate that commercial production is exposed and distributed locally, it may be necessary to estimate consumption in order to include it in the exposure of local populations;

- total risk, including the risk associated with the background concentration, in addition to the risk attributable to local pollution sources studied. It is then necessary to take account of exposure associated with the pollutant concentration in local products due to the background concentration and exposure associated with food produced outside the site's impact zone. Concentrations in these foods can be found from national surveys in product contamination (surveys by the French government food department and department for competition, consumers and repression of fraud, INERIS report DRC-08-94882-15772A).

Plants are the input link to the food chain. A large number of plant species present on a site can be consumed by people or animals, or can be used for environmental monitoring. For want of data, they cannot all be studied. They must therefore be grouped into different categories based on their modes of contamination and consumption data.

In this way we can distinguish:

- root vegetables,
- tuber vegetables,
- leaf vegetables,
- fruit vegetables and fruit,
- seeds (cereals, fruit and dry vegetables),
- fodder,
- silage (type: maize silage).

The number of plant categories finally considered in a study depends on the degree of specificity and desired accuracy.

Contamination of plants can result from different phenomena:

- direct uptake from the soil, following which the pollutant is distributed within the plant by convection (associated with evapotranspiration) and diffusion,
- particulate deposition of pollutant from the atmosphere,
- deposition of particles from the soil after being suspended by the wind, rain, etc.,
- absorption of gaseous pollutant (for organic pollutants) from the atmosphere,
- transfer from irrigation water.

The general approach is to sum contributions associated with these different phenomena, as if they were independent:

$$C_p = C_{rp} + C_{dap} + C_{dsp} + C_{gp} + C_{ip}$$

Equation 1.6.1

Symbol	Parameter	Dimensions	Units	Status
C_p	Concentration in the plant	M.dry M^{-1}	mg.dry kg^{-1}	C or E
C_{rp}	Concentration in the plant due to direct uptake from the soil	M.dry M^{-1}	mg.dry kg^{-1}	C or E
C_{dap}	Concentration in the plant due to particle deposition from the atmosphere	M.dry M^{-1}	mg.dry kg^{-1}	C or E
C_{dsp}	Concentration in the plant due to deposition of particles from the soil	M.dry M^{-1}	mg.dry kg^{-1}	C or E
C_{gp}	Concentration in the plant due to absorption of gaseous pollutant	M.dry M^{-1}	mg.dry kg^{-1}	C or E
C_{ip}	Concentration in the plant due to irrigation by spraying	M.dry M^{-1}	mg.dry kg^{-1}	C or E

Summing in this way is a classical approach in most multimedia exposure models (HHRAP, US EPA, 2005; ERWYN; CLEA, The Environment Agency, 2002; HESP, Shell Global solutions, 1995; CalTOX exposure model, University of California, 1993, 1997). However, contamination by diffusion from the soil or air depends on the pollutant concentration in the plant, and independently estimating the impact of different contamination processes can overestimate concentrations in the plant.

There are compartmental models where the concentration in the plant is calculated from a mass balance taking account of the different inflows to the plant (pollutant flux from the soil, pollutant flux from the air), loss phenomena experienced by the plant (flux from the leaves into the air, metabolism, dilution by growth of the plant, photo-degradation, etc.), as well as distribution mechanisms within this plant (flux from the leaves to other parts of the plant, etc.). But these models (CalTOX transfer modules, University of California, 1993, 1997, Mckone et al., 2002; PlantX, Trapp et al., 1994; Paterson et al., 1994) require a large number of parameters to be defined for different plant categories (eg. surface area and volume of leaves, conductance of the cuticle, metabolic rate, xylem flux, phloem flux, etc.). They are not discussed here. Some of them have been covered in a detailed presentation (INERIS, 2002d).

1.6.1. CONCENTRATION IN THE PLANT ASSOCIATED WITH DIRECT UPTAKE FROM THE SOIL

Pollutants are transported in the soil solution as far as the area around the roots by convection and diffusion. They are taken up by the plant passively and/or actively by the roots. The contamination of other parts of plants from the roots takes place through the rising sap flux (xylem).

However, it is useful to note that in the case of belowground vegetables, there can also be direct pollutant uptake from the soil by diffusion through the tissues of the part eaten, without passing through the roots (eg. potatoes) (Trappe et al., 2007).

The pollutant concentration in the plant associated with direct uptake from the soil is estimated from a bioconcentration coefficient (B_r) that represents the ratio between the pollutant concentration in the plant and the pollutant concentration in the soil.

$$C_{rp}(T_{récolte}) = B_r \times \overline{C}_{s,t_{pl} \to t_{réc}}$$

Equation 1.6.2

Symbol	Parameter	Dimensions	Units	Status
$C_{rp}(T_{récolte})$	Pollutant concentration in the plant associated with direct uptake from the soil, at the time of harvest	M.dry M^{-1}	mg.dry kg^{-1}	C or E
$\overline{C}_{s,t_{pl} \to t_{réc}}$	Average pollutant concentration in the soil during the growing period	M.M^{-1}	mg.kg^{-1}	C or E
B_r	Soil-plant bioconcentration coefficient	M of soil.dry M^{-1} of plant	kg of soil.dry kg^{-1} of plant	C or E

The pollutant concentration in the soil should correspond to the area covered by the roots of the plants considered. The average pollutant concentration over the corresponding soil depth Z_s can be estimated from the equations developed in section 1.1.2.

The difficulty of the approach presented in this section lies in defining the bioconcentration coefficient (B_r). Very different values for B_r can be found in the literature. The value of B_r depends particularly on:

- the substance, its speciation, its concentration in the soil,
- the physico-chemical characteristics of the soil (pH, organic carbon content, cationic exchange capacity, etc.),
- other substances present in the soil,
- the plant type, species and plant part considered.

Of the best practice rules for defining values of B_r the most suitable will be reviewed in future documents covering the definition of physico-chemical parameters and transfer coefficients for substances. Despite these rules, it is worth remembering that this type of parameter remains blighted by variability and generally substantial uncertainty.

In addition, while data relating to some metals is plentiful, the available data for some organic substances are very rare or even non-existent, hence the frequent recourse to empirical relationships (Quantitative Structure-Activity Relationship: QSAR) that can be used to define the coefficient B_r from a known parameter of the substance. For organic substances, it is often the octanol-water partition coefficient (K_{ow}).

Depending on the available data, the concentration in the plant associated with direct uptake from the soil can also be expressed relative to the pollutant concentration in the soil water, or to the so-called 'exchangeable' pollutant fraction in the soil. Therfore, we have to be careful that the bioconcentration coefficient used is consistent with the expression for the pollutant concentration in the soil.

If the bioconcentration coefficient ($B_{r'}$) corresponds to the ratio of the concentration in the plant over the pollutant content in the soil water, we can state:

$$C_{rp}(T_{récolte}) = \frac{B_{r'}}{t_{sp}} \times \overline{C}_{es, t_{pl} \rightarrow t_{réc}}$$

Equation 1.6.3

Yet, according to equation 1.1.11 (conditions: pollutant concentration in the soil below the limit of solubility, multi-phase equilibrium reached between the different phases in the soil),

$$C_{es} = \frac{C_s \times MV_s}{MV_s \times K_d + \theta + \alpha \times \dfrac{H}{R \times T_s}}$$

Equation 1.6.4

where K_d: partition coefficient between soil particles and soil water,

θ: volume fraction occupied by soil water,

α: volume fraction occupied by soil air,

H: Henry constant,

R: universal gas constant,

T_s: soil temperature,

MV_s: bulk soil density.

If $\quad \alpha \times \dfrac{H}{R \times T_s} \ll \theta + MV_s \times K_d$

then $\quad C_{rp}(T_{récolte}) = \dfrac{B_{r'}}{t_{sp}} \times \dfrac{MV_s}{MV_s \times K_d + \overline{\theta}_{t_{pl} \rightarrow t_{réc}}} \times \overline{C}_{s, t_{pl} \rightarrow t_{réc}}$

Equation 1.6.5

and $\quad B_r = \dfrac{B_{r'}}{t_{sp}} \times \dfrac{MV_s}{MV_s \times K_d + \overline{\theta}_{t_{pl} \rightarrow t_{réc}}}$

Equation 1.6.6

Symbol	Parameters	Dimensions	Units	Status
$C_{rp}(T_{récolte})$	Pollutant concentration in the plant associated with direct uptake from the soil, at the time of harvest	M.dry M^{-1}	mg.dry kg^{-1}	C or E
$B_{r'}$	Soil water-plant bioconcentration coefficient expressed relative to the weight of fresh matter in the plant	Water L^3.fresh M^{-1} of plant	Water m^3.fresh kg^{-1} of plant	C or E
B_r	Soil-plant bioconcentration coefficient expressed relative to the weight of dry matter in the plant	M of soil.dry M^{-1} of plant	kg of soil.dry kg^{-1} of plant	C or E

t_{sp}	Dry matter content of the plant	-	-	E
$\overline{C}_{s,t_{pl}\rightarrow t_{réc}}$	Average pollutant concentration in the soil during the growing period	$M.M^{-1}$	$mg.kg^{-1}$	C or E
$\overline{C}_{es,t_{pl}\rightarrow t_{réc}}$	Average pollutant concentration in the soil water during the growing period	$M.L^{-3}$	$mg.m^{-3}$	C or E
MV_s	Bulk soil density	$M.L^{-3}$	$kg.m^{-3}$	E
K_d	Partition coefficient between soil particles and soil water	$L^3.M^{-1}$	$m^3.kg^{-1}$	C or E
$\overline{\theta}_{t_{pl}\rightarrow t_{réc}}$	Volume fraction occupied by the soil water during the growing period	-	-	E

1.6.2. CONCENTRATION IN THE PLANT ASSOCIATED WITH PARTICLE DEPOSITION FROM THE ATMOSPHERE

This sections focuses on particle deposition associated with an atmospheric source (this may be emissions from a local source or conversely from widely-spread sources located at large distances appearing in the background concentration). It does not consider the deposition of particles coming from the soil or resuspended from the soil (covered in section 1.6.4).

The concentration in the plant is modelled by considering continuous deposition of particles on the plant and losses associated with the action of wind and rain.

There are two available approaches for estimating the resulting concentration in the plant:

- the first is to estimate direct deposition on the edible parts of the plant. Under this approach, only parts of the plant in contact with the atmosphere can be affected by atmospheric fallout. This transfer mechanism therefore affects fodder, leaf vegetables, fruit and unprotected fruit vegetables, such as strawberries or tomatoes. Conversely, according to this approach, belowground vegetables, seeds, fruit and fruit vegetables protected by a shell (such as nuts or dried beans) are not affected. This is the approach most frequently used in models dedicated to chemical pollutants (cf. HHRAP, US EPA, 2005; MPE, US EPA, 1998; HARP, CalEPA, 2003).

- the second considers particle deposition on the leaves of the plant then transfer of the substance to the edible parts. In other words, the substance initially deposited on the surface of leaves is absorbed and transported to other parts of the plant. According to this approach, all parts of the plant are potentially affected by contamination from atmospheric deposition. However, the rate of transfer can be very slow, even nil, depending on the substance or plant part considered. This approach is used in radioecology (cf. ECOSYS-87, Müller et al., 1993; RESRAD, US DOE, 2001; ERWYN, US DOE, 2003; GRNC, 2002).

1.6.2.1. ESTIMATES FROM DEPOSITION ON EDIBLE PARTS

1.6.2.1.1. CALCULATION OF PARTICULATE DEPOSITION

Calculating the concentration from particulate deposition takes account of dry particulate deposition (D_{psp}) and wet particulate deposition (D_{php}).

Dry deposition is assumed to have better adhesion to plants than wet deposition, part of which is removed immediately.

$$D_{pp} = D_{psp} + F_h \times D_{php}$$

Equation 1.6.7

Symbol	Parameters	Dimensions	Units	Status
D_{pp}	Particulate deposition on plants	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
D_{psp}	Dry particulate deposition	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	E
D_{php}	Wet particulate deposition	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	E
F_h	Fraction of wet particulate deposition that adheres on plants	-	-	E

F_h can take different values depending on the chemical form of the pollutant (cf. INERIS, 2008b; US EPA, 2005 and future documents on the values of physico-chemical parameters of substances).

Dry particulate deposition (D_{psp}) and wet particulate deposition (D_{php}) can be calculated from atmospheric dispersion models (cf. section 1.1.2.2.1).

1.6.2.1.2. CALCULATING CONCENTRATION IN THE EDIBLE PARTS OF THE PLANT

The pollutant concentration attributable to particulate deposition is based on the following equations:

$$\frac{dm_{dap}}{dt} = S \times D_{pp} \times I - \lambda_w \times m_{dap}$$

Equation 1.6.8

where D_{pp}: particulate deposition on plants,

m_{dap}: mass of pollutant in particulate phase deposited on the edible parts of plants by atmospheric deposition,

S: surface area of the cultivated zone considered,

I: interception fraction for the edible parts of the plant. This coefficient takes account of the fact that all the atmospheric particles are not deposited on the plant. It represents the fraction of deposition intercepted by the edible parts of plants out of the total deposition,

λ_w: coefficient for loss by the action of rain and wind (this parameter can also take photo-degradation at the surface of the plant into account).

hence $M_v \times \dfrac{dC_{dap}}{dt} + C_{dap} \times \dfrac{dM_v}{dt} = S \times D_{pp} \times I - \lambda_w \times M_v \times C_{dap}$

Equation 1.6.9

and $\dfrac{dC_{dap}}{dt} = \dfrac{D_{pp} \times I}{P_r} - \lambda_w \times C_{dap} - \dfrac{dM_v}{M_v dt} \times C_{dap}$

Equation 1.6.10

where C_{dap}: concentration in the edible parts of the plant,

M_v: mass of edible plant products,

P_r: plant productivity (mass of edible plant products per unit cultivated surface area).

If plant growth can be approximated by an exponential function (as is the case for leaves in vegetative growth phase (Trapp et al., 1997)) then,

$$\frac{dM_v}{M_v \cdot dt} = \lambda_c$$

Equation 1.6.11

and $\dfrac{dC_{dap}}{dt} = \dfrac{D_{pp} \times I}{P_r} - (\lambda_c + \lambda_w) \times C_{dap}$

Equation 1.6.12

where λ_c: growth rate of plant products,

The sum $(\lambda_w + \lambda_c)$ is generally replaced by a loss coefficient Λ.

For continuous pollutant deposition on the consumed parts of the plant, these equations have to be integrated from the start to the end of the plant's exposure period, the end of the exposure period generally being corresponding to harvest.

1. Cases where parameters of the equation are not constant

The plant concentration due to particulate deposition can be estimated by integrating the equation over successive time intervals (Δt) from the beginning of the exposure period to atmospheric deposition (time of germination for fodder or leaf vegetables, time of fruiting for fruits and seeds), until the time of harvest. In this case, the simplest approach is to use equation 1.6.8.

From this equation we deduce:

$$\frac{dC_{dap\_s}}{dt} = D_{pp} \times I - \lambda_w \times C_{dap\_s} \qquad \text{Equation 1.6.13}$$

where C_{dap_s}: mass of pollutant in the edible parts of the plant per unit cultivated surface area (M.L^{-2}).

$$\text{hence } C_{dap\_s}(t) = C_{dap\_s}(t - \Delta t) \times e^{-\lambda_w \times \Delta t} + \frac{D_{pp} \times I}{\lambda_w} \times \left(1 - e^{-\lambda_w \times \Delta t}\right) \qquad \text{Equation 1.6.14}$$

$$\text{and } C_{dap}(T_{récolte}) = \frac{C_{dap\_s}(T_{récolte})}{P_r(T_{récolte})} \qquad \text{Equation 1.6.15}$$

Symbol	Parameters	Dimensions	Units	Status
$C_{dap}(T_{récolte})$	Pollutant concentration in the edible parts of the plant at the time of harvest	M.dry M^{-1}	mg.dry kg^{-1}	C or E
C_{dap_s}	Mass of pollutant in the edible parts of the plant per unit cultivated surface area	M.soil L^{-2}	mg.soil m^{-2}	C or E
D_{pp}	Particulate deposition on plants	M.L^{-2}.T^{-1}	m^{-2}.s^{-1}	C or E
I	Interception fraction for the edible parts of the plant	-	-	E
λ_w	Pollutant loss coefficient by the action of rain and wind (even photo-degradation)	T^{-1}	s^{-1}	E
$P_r(T_{récolte})$	Plant productivity at harvest, also called crop yield	Dry M.L^{-2}	Dry kg.m^{-2}	E

2. Cases where deposition and the loss coefficient are assumed constant

Within chronic risk assessment studies associated with ICPEs, emissions are assumed to be constant and the impact of facilities is estimated from an average deposition D_{pp}, constant over time, even if this deposition varies with the weather conditions. Similarly, the coefficient λ_w, which is intended to take account of the reduction in the quantity of particles deposited on leaves due to the action of wind and rain, varies according to the weather conditions, but given the available data it is usually estimated using a constant value of the entire exposure period of the plant.

In most models devoted to assessing risks where atmospheric deposition of particles on plants is taken into account in this way, the pollutant concentration due to this transfer is estimated by integrating equation 1.6.12 over the entire exposure period to atmospheric deposition, although the interception fraction (I) and plant productivity (P_r) tend to increase over time. An expression in the following form is then supplied:

$$C_{dap}(T_{récolte}) = \frac{D_{pp} \times I}{P_r(T_{récolte}) \times \Lambda} \times \left(1 - e^{-\Lambda(T_{récolte})}\right)$$

Equation 1.6.16

This expression is based on two approximations:

- **exponential plant growth.** If this approximation is acceptable for certain leaf vegetables such as lettuces, for fruits or fruit vegetables with a relatively long ripening phase, this approximation seems more debatable;

- **a constant I / P_r ratio over time.**

  For grass on pastureland continuously-grazed by animals, this relationship can be assumed constant. However, for plants harvested at the end of vegetative growth or at maturity, this assumption appears inappropriate.

The uncertainties associated with expression 1.6.16 are currently poorly understood. Excluding the case of pasture grass, it is therefore preferable to estimate the concentration in the edible parts of plants from equations 1.6.14 and 1.6.15.

In the absence of information to define the interception fraction (I) as a function of time, or to avoid a time-increment approach, equation 1.6.13 may be integrated by assigning I a constant value equal to its maximum value (generally its value at the time of harvest).

$$C_{dap}(T_{récolte}) = \frac{D_{pp} \times I(T_{récolte})}{P_r(T_{récolte}) \times \lambda_w} \times \left(1 - e^{-\lambda_w \times T_{récolte}}\right)$$

Equation 1.6.17

Symbol	Parameters	Dimensions	Units	Status
$C_{dap}(T_{récolte})$	Pollutant concentration in the edible parts of the plant at the time of harvest	M.dry M^{-1}	mg.dry kg^{-1}	C or E
D_{pp}	Particulate deposition on plants	M.L^{-2}.T^{-1}	m^{-2}.s^{-1}	C or E
$I(T_{récolte})$	Interception fraction for the edible parts of the plant at the time of harvest	-	-	E
λ_w	Pollutant loss coefficient by the action of rain and wind (even photo-degradation)	T^{-1}	s^{-1}	C or E
$P_r(T_{récolte})$	Plant productivity at harvest, also called crop yield	Dry M.L^{-2}	Dry kg.m^{-2}	E

Comment: The simplified approach above, based on using the interception value at the time of harvest, overestimates $C_{dap}(T_{récolte})$. Conversely, using a representative value for the average of I over the entire exposure period to atmospheric deposition, as in some models, leads to an approximation in which we do not know if it tends to underestimate or overestimate $C_{dap}(T_{récolte})$, a situation that can be awkward for drawing conclusions.

1.6.2.2. ESTIMATING FROM DEPOSITION ON THE FOLIAR PART AND TRANSFER TO THE PARTS CONSUMED

This second approach was developed for radionuclides and can be applied to a certain number of metals, for which data relating to translocation are available.

This approach also takes dry deposition and wet deposition into account. The 'interception fraction' parameter is replaced by a parameter called 'capture ratio'. A capture ratio is thus defined for dry deposition and another for wet deposition.

1.6.2.2.1. CALCULATING CONCENTRATION IN THE FOLIAR PART

Expressions similar to equations 1.6.10 and 1.6.13 can be used to estimate the concentration in the leaves of plants.

$$\frac{dC_{dap}}{dt} = \frac{D_{psp} \times R_{c,s} + D_{php} \times R_{c,h}}{B_v} - \lambda_w \times C_{dap} - \frac{dM_v}{M_v} \times C_{dap}$$
Equation 1.6.18

or $\quad \frac{dC_{dap\_s}}{dt} = D_{psp} \times R_{c,s} + D_{php} \times R_{c,h} - \lambda_w \times C_{dap\_s}$
Equation 1.6.19

where $R_{c,s}$: dry capture ratio,

$\quad R_{c,h}$: wet capture ratio,

$\quad B_v$: plant biomass at the soil surface.

1. If the parameters for equation 1.6.19 are not constant, integrating over successive time intervals (Δt) (from germination to the time of harvest gives for the leaves:

$$C_{dap\_s}(t) = C_{dap\_s}(t - \Delta t) \times e^{-\lambda_w \times \Delta t} + \frac{D_{psp} \times R_{c,s} + D_{php} \times R_{c,h}}{\lambda_w} \times \left(1 - e^{-\lambda_w \times \Delta t}\right)$$
Equation 1.6.20

and $\quad C_{dap}(T_{récolte}) = \frac{C_{dap\_s}(T_{récolte})}{B_v(T_{récolte})}$
Equation 1.6.21

Symbol	Parameters	Dimensions	Units	Status
C_{dap} ($T_{récolte}$)	Pollutant concentration in the foliar part of plants at the time of harvest	M.dry M^{-1}	mg.dry kg^{-1}	C or E
C_{dap_s}	Pollutant concentration in the foliar part of plants per unit cultivated surface area	M.soil L^{-2}	mg.soil m^{-2}	C or E
D_{psp}	Dry particulate deposition on plants	M.L^{-2}.T^{-1}	m^{-2}.s^{-1}	C or E
D_{php}	Wet particulate deposition on plants	M.L^{-2}.T^{-1}	m^{-2}.s^{-1}	C or E
$R_{c,s}$	Dry capture ratio	-	-	E
$R_{c,h}$	Wet capture ratio	-	-	E
λ_w	Pollutant loss coefficient by the action of rain and wind (even photo-degradation)	T^{-1}	s^{-1}	E
B_v($T_{récolte}$)	Plant biomass above the soil at the time of harvest	Dry M.L^{-2}	Dry kg.m^{-2}	E

2. **With the same approximations as in the approach using direct deposition on the edible parts of plants**, by assuming $\dfrac{D_{psp} \times R_{c,s} + D_{php} \times R_{c,h}}{B_v}$,

λ_w constant and exponential growth of the plant biomass, equation 1.6.18 is often integrated over the entire period to atmospheric deposition to obtain the following relationship for leaves:

$$C_{dap}(T_{récolte}) = \frac{D_{psp} \times R_{c,s} + D_{php} \times R_{c,h}}{\Lambda \times B_v(T_{récolte})} \times \left(1 - e^{-\Lambda \times T_{récolte}}\right)$$
Equation 1.6.22

where Λ: loss coefficient ($\Lambda = \lambda_w + \lambda_c$),

λ_c: growth rate of plant products.

Here again, the assumption of a constant ratio $\dfrac{D_{psp} \times R_{c,s} + D_{php} \times R_{c,h}}{\Lambda \times B_v(T_{récolte})}$ over time

seems inappropriate, apart from pastureland. Equations 1.6.20 and 1.6.21 are most suitable.

As part of a simplified approach, if we do not have data to define $R_{c,s}$ and $R_{c,h}$ over time or to avoid a time-increment calculation, equation 1.6.18 can be integrated, assigning $R_{c,s}$ and $R_{c,h}$ constant values equal to their maximum values (specifically, $R_{c,s}(T_{récolte})$ and $R_{c,h}(T_{récolte})$). This approach tends to overestimate $C_{dap}(T_{récolte})$.

$$C_{dap}(T_{récolte}) = \frac{D_{psp} \times R_{c,s}(T_{récolte}) + D_{php} \times R_{c,h}(T_{récolte})}{\lambda_w \times B_v(T_{récolte})} \left(1 - e^{-\lambda_w \times T_{récolte}}\right)$$
Equation 1.6.23

Symbol	Parameters	Dimensions	Units	Status
C_{dap} ($T_{récolte}$)	Pollutant concentration in the foliar part of plants	M.dry M^{-1}	mg.dry kg^{-1}	C or E
D_{psp}	Dry particulate deposition on plants	M.L^{-2}.T^{-1}	m^{-2}.s^{-1}	C or E
D_{php}	Wet particulate deposition on plants	M.L^{-2}.T^{-1}	m^{-2}.s^{-1}	C or E
$R_{c,s}$	Dry capture ratio	-	-	E
$R_{c,h}$	Wet capture ratio	-	-	E
λ_w	Pollutant loss coefficient by the action of rain and wind (even photo-degradation)	T^{-1}	s^{-1}	C or E
B_v ($T_{récolte}$)	Plant biomass above the soil at the time of harvest	Dry M.L^{-2}	Dry kg.m^{-2}	E

1.6.2.2.2. CALCULATING CONCENTRATIONS IN OTHER PARTS OF THE PLANT

After deposition on the leaves and absorption by the plant, contaminants can be transferred to other parts of the plant. The term 'translocation' is used here to mean the transfer of contaminants from leaves to the parts consumed.

The translocation coefficient is the ratio of the concentration in a tissue, in this case the edible part, over the pollutant quantity retained on the foliage per square metre at the moment of deposition, or:

$$\frac{dC_{dap\_s}}{dt} = \left(D_{psp} \times R_{c,s} + D_{php} \times R_{c,h}\right) \times T_r$$
Equation 1.6.24

where T_r: translocation coefficient for the pollutant from the leaf to the edible parts.

Integrating by time increments gives:

$$C_{dap}(T_{récolte}) = \frac{1}{P_r(T_{récolte})} \sum_{i=1}^{n} \left(D_{psp}(t_i) \times R_{c,s}(t_i) + D_{php}(t_i) \times R_{c,h}(t_i) \right) \times T_r(t_i) \times \Delta t_i$$

Equation 1.6.25

where i: iteration number between 1 and n,

and $\quad \sum_{i=1}^{n} \Delta t_i = T_{récolte} - T_{exp,veg}$

Symbol	Parameters	Dimensions	Units	Status
C_{dap} ($T_{récolte}$)	Pollutant concentration in the edible parts of the plant at the time of harvest	M.dry M^{-1}	mg.dry kg^{-1}	C or E
D_{psp}	Dry particulate deposition on plants	M.L^{-2}.T^{-1}	m^{-2}.s^{-1}	C or E
D_{php}	Wet particulate deposition on plants	M.L^{-2}.T^{-1}	m^{-2}.s^{-1}	C or E
$R_{c,s}$	Dry capture ratio	-	-	E
$R_{c,h}$	Wet capture ratio	-	-	E
T_r	Translocation coefficient	-	-	E
P_r ($T_{récolte}$)	Plant productivity at harvest, also called crop yield (mass of edible plant products per unit cultivated surface area)	Dry M.L^{-2}	Dry kg.m^{-2}	E
$T_{exp,vég}$	Start date of plant exposure to deposition (germination)	T^{-1}	s^{-1}	E
$T_{récolte}$	Harvest date	T^{-1}	s^{-1}	E

As it is, using this equation is made difficult by the lack of data to define the translocation coefficient. In practice, empirical values have been defined for a few radionuclides. T_r depends especially on the element in question, the plant species, its stage of development (the translocation process is more significant from the fruit formation period to te ripening period).

In existing models (GCNC, 2002; RESRAD, US DOE, 2001; ERMYN, US DOE, 2003), the most frequently-used equation to estimate the concentration in the edible parts after deposition on the leaves and translocation, is of the type:

$$C_{dap}(T_{récolte}) = \frac{\left(D_{psp} \times R_{c,s} + D_{php} \times R_{c,h} \right) \times T_r}{P_r(T_{récolte})} \times \left(1 - e^{-\Lambda \times T_{récolte}} \right)$$

Equation 1.6.26

In this case, the concentration in the edible parts is estimated from the concentration remaining on the leaves at the time of harvest. The definition of T_r is therefore different to that given above.

Studies where a translocation coefficient is measured may also use variable protocols and the significance attributed to this parameter can therefore be different in different cases. We should therefore be cautious about the suitability of the method of defining the value attributed to T_r to the equation used to calculate pollutant concentrations in the edible parts of plants.

1.6.2.3. COMPARISON OF TWO ESTIMATION APPROACHES

For leaf vegetables and fodder, since the edible part is the part directly exposed, the two approaches (direct deposition on the edible parts and deposition on the leaves followed by transfer to the edible parts) are very similar. Only the definition of the wet deposition fraction initially intercepted by the plant differs.

The two approaches give the same results if:

$$R_{c,s} = I \qquad \text{Equation 1.6.27}$$

and $R_{c,h} = F_w \times I$ Equation 1.6.28

For fruits, cereal and root vegetables, IRSN (GCNC, 2002) reported values of about 0.1 for radionuclides considered as mobile (such as those of cadmium, nickel, zinc, selenium or antimony) and values between 0 and 0.02 are given for radionuclides said to be relatively immobile (such as those of manganese or lead). Under these conditions, the two approaches (direct deposition on the edible parts and deposition on the foliar parts followed by translocation), for root vegetables and elements corresponding to these relatively immobile radionuclides, give a concentration associated with particulate deposits equal to zero. In other cases (fruits, seeds, root vegetables for elements corresponding to radionuclides considered as mobile), the results of the two approaches can be different.

While the concept of deposition on the leaves appears more appropriate when fruits are covered by the plants' leaves, and while disregarding transfer from the from the leaves to the storage organs in the first approach can appear as a drawback, defining the translocation coefficient as required by the second approach is itself tricky, given there is the little amount of data available.

As far as we know, there is no study where the two calculation methods (direct deposition on the edible parts and deposition on the foliar part followed by translocation to the edible parts) have been compared. Experimental studies show that, depending on the mobility of the pollutant and the vegetative stage of the plant at the moment of contamination, one or other of the processes (either direct deposition on the fruit or deposition on the leaves and translocation) may predominate. Under these conditions, it is difficult to recommend one modelling approach compared to the other.

1.6.3. CONCENTRATION IN THE PLANT ASSOCIATED WITH ABSORPTION OF GASEOUS POLLUTANT

There are two approaches for estimating this transfer:

- one based on using an empirical bioconcentration coefficient,
- the other based on calculating gaseous deposition.

1.6.3.1. CALCULATION BASED ON THE AIR-PLANT BIOCONCENTRATION COEFFICIENT

$$C_{gp}(T_{récolte}) = \frac{B_f}{t_{ps}} \times \overline{C}_{ag,t_{exp,veg} \to t_{réc}} \qquad \text{Equation 1.6.29}$$

where $C_{gp}(T_{récolte})$: concentration in the plant at the time of harvest due to absorption of gaseous pollutant,

B_f: air-plant bioconcentration coefficient. The air-plant bioconcentration coefficient is the ratio of the concentration in the part of the plant considered over the concentration in the air,

t_{ps}: dry matter content of the plant,

$\overline{C}_{ag,t_{exp,veg} \to t_{réc}}$: average pollutant concentration in the air in gaseous form during the exposure period of the plant organ considered.

If the gaseous fraction in the air is constant over time, then:

$$C_{gp}(T_{récolte}) = \frac{B_f}{t_{ps}} \times \overline{C}_{a,t_{exp,veg} \to t_{réc}} \times F_v \qquad \text{Equation 1.6.30}$$

Symbol	Parameters	Dimensions	Units	Status
$C_{gp}(T_{récolte})$	Concentration in the plant at the time of harvest associated with absorption of gaseous pollutant	M.dry M^{-1}	mg.dry kg^{-1}	C or E
F_v	Pollutant fraction in gaseous form	-	-	C or E
$\overline{C}_{ag,t_{exp,veg} \to t_{réc}}$	Average pollutant concentration in the air in gaseous form from the beginning of the exposure period of the plants to atmospheric pollutants (germination date for fodder or leaf vegetables, fruiting date for fruits and seeds) to the time of harvest	M.L^{-3}	mg.m^{-3}	C or E
$\overline{C}_{a,t_{exp,veg} \to t_{réc}}$	Average pollutant concentration in the air in gaseous and particulate forms from the beginning of the exposure period of the plants to atmospheric pollutants (germination date for fodder or leaf vegetables, fruiting date for fruits and seeds) to the time of harvest	M.L^{-3}	mg.m^{-3}	C or E
B_f	Air-plant bioconcentration coefficient	Air L^3 .fresh M^{-1} of plant	Air m^3.fresh kg^{-1} of plant	C or E
t_{sp}	Dry matter content of the plant	-	-	E

1.6.3.2. Calculation from gaseous deposition

As when calculating the pollutant concentration in the plant associated with particulate deposition, the concentration associated with gaseous deposition results from a gain: the deposition and a loss, which can be associated with degradation of the substance or its volatilisation.

If the terms in the equation are considered constant over time, we can state:

$$C_{gp}(T_{récolte}) = \frac{D_{gp} \times (1 - e^{-\lambda_f \times T_{récolte}})}{\lambda_f \times P_r(T_{récolte})} \qquad \text{Equation 1.6.31}$$

Symbol	Parameters	Dimensions	Units	Status
$C_{gp}(T_{récolte})$	Concentration in the plant at the time of harvest associated with absorption of gaseous pollutant	M.dry M^{-1}	mg.dry kg^{-1}	C or E
$P_r(T_{récolte})$	Plant productivity at the time of harvest (or crop yield)	Dry $M.L^{-2}$	Dry $kg.m^{-2}$	C or E
λ_f	Loss coefficient by volatilisation and/or degradation	T^{-1}	s^{-1}	E
D_{gp}	Gaseous deposition on the plant	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E

Smith et al. (1995) and Trapp et al. (1997) propose two different methods to estimate gaseous deposition on the leaves of a plant (D_{gp}).

According to Trapp et al., it can be stated:

$$D_{gp} = A_f \times g_f \times C_{ag}$$ Equation 1.6.32

where g_f: conductance of the plants' leaves,

A_f: foliar index (foliar surface area per unit surface area occupied at the soil),

C_{ag}: gaseous pollutant concentration in the air.

Smith et al. give the following expression:

$$D_{gp} = v_{dgp} \times C_{ag} \times I_g$$ Equation 1.6.33

where I_g: fraction of the gaseous deposition intercepted by the leaves,

v_{dgp}: gaseous deposition velocity on the plants' leaves,

$$v_{dgp} = \frac{1}{r_a + r_b + r_c}$$ Equation 1.6.34

where r_a: aerodynamic resistance of the atmospheric layer,

r_b: resistance of the sub-layer, i.e. of the very thin layer of stagnant air above the leaf,

r_c: resistance of the leaves. r_c depends on the plant cover density, absorption capacity via the stomata, leaf surface type (smooth or otherwise), humidity, etc.

1.6.3.3.   COMPARISON OF THE TWO APPROACHES

The two approaches above have disadvantages associated with the difficulty of establishing their parameters. Little data exist to define:

- the bioconcentration coefficient (B_f) for the first approach,
- the gaseous deposition velocity on the plants (v_{dgp}), conductance of the leaves (g_f) and rate of loss (λ_f) for the second approach.

However, for polychlorodibenzodioxins and polychlorodibenzofurans (PCDD/PCDF), values of transfer coefficients have been defined using measurement data from the scientific literature (INERIS, 2004b).

For these substances, US EPA (1998, 2004c) has also compared the two approaches presented above with field data. These are data from a study, conducted between 1992 and 1993 in the United Kingdom, combining measurements of deposition and concentration in air and in grass. Two sets of data were used, one for a rural environment and the other for an industrial environment. The profile of the different concentrations measured in the rural environment correctly correlated with the approach using bioconcentration coefficients; however, the concentrations were underestimated by a factor of about 2. Performance of the model appeared to be not so good for data

collected in the industrial environment (underestimated by a factor of 3). The decision not to take contamination of the grass with the re-suspended soil particles may explain these results. For the model based on gaseous deposition on plants, the two means of estimating D_{gp} presented above have been tested, but this model gave even lower results, with estimated concentrations 2 to 4 times less than those obtained with bioconcentration coefficients.

For PCDDs and PCDFs, it is therefore recommended to use the approach based on bioconcentration coefficients. For other pollutants, the choice is less obvious given the scarce data available to define air-plant bioconcentration coefficients. There is an empirical relationship giving the air-plant bioconcentration coefficient based on the octanol-water partition coefficient (B_f) and the Henry constant (H) of pollutants, but it seems to overestimate bioconcentration coefficients (cf. US EPA, 2005 and future documents on the physico-chemical and transfer parameters of substances).

Finally, to define an appropriate value for this parameter from the scientific literature, it is important to pay particular attention to the conditions under which the data are obtained, as for other bioconcentration or transfer coefficients. Available data for the air-plant bioconcentration coefficient generally relate to the leaves. It appears that these data are not appropriate for plant products with a lower specific surface area, such as fruit vegetables or fruits. Semi-volatile and bioaccumulable organic substances, such as dioxins or polychlorobiphenyls, are generally unsuited to migrating from the surface to the interior of the plant. In addition, we recommend multiplying the measured bioconcentration coefficient for a leaf by a correction factor (can be estimated as the ratio of the surface area per unit weight of the vegetable or fruit considered over the surface area per unit weight of the leaf) before using equations 1.6.29 or 1.6.31.

1.6.4. CONCENTRATION IN THE PLANT ASSOCIATED WITH DEPOSITION OF PARTICLES FROM THE SOIL

Pollutants adsorbed to soil particles can be resuspended by action of the wind or mechanical actions. Splashes caused by the rain ('rainsplash' in the scientific literature) also contribute to plant contamination by soil particles.

When there is little root uptake of pollutants, deposition of soil particles on the surface of plants can be the predominant means of contaminating the organs of plants located above the soil (eg. dioxins, for which the contamination of leaves, fruits and seeds by root uptake is most frequently considered as nil). Thus, work by Kryshev (1992), cited in the PNNL document (2006) shows that, around Chernobyl, splashes of soil particles due to the rain represent 60 to 70% of the contamination on the lower parts of cereals and perennial grasses.

There are two approaches for taking deposition of soil particles on plants into account:

- the first consists of defining a percentage by weight of soil particles attached to the plant, that cannot be removed by traditional washing of plants, as done before they are eaten;
- the second consists of modelling the concentration of particles resuspended in the air, then modelling deposition of the particles on plants, following the same approach as used to estimate direct deposition of atmospheric particles on plants (cf. section 1.6.2).

1.6.4.1. USING THE FRACTION OF PARTICLES ATTACHED TO THE PLANT

This is the simplest approach: the impact of all the factors involved is combined using a single parameter (plant height, foliage type, wind and rain intensity, soil type). This approach is used in models such as CLEA (The Environment Agency, 2002), CSOIL (RIVM, 2007), BIOMASS (IAEA, 2000) and EPRI (Smith et al., 1996).

According to this approach:

$$C_{dsp}(T_{récolte}) = R_{sp} \times \overline{C}_{s,t_{exp,veg} \to t_{réc}}$$

Equation 1.6.35

Symbol	Parameters	Dimensions	Units	Status
$C_{dsp}(T_{récolte})$	Concentration in the plant due to deposition of particles from the soil, at the time of harvest	M.dry M^{-1}	mg.dry kg^{-1}	C or E
$\overline{C}_{s,t_{exp,veg} \to t_{réc}}$	Average pollutant concentration in the soil at the beginning of the exposure period of the plants to deposition (germination date for fodder or leaf vegetables, fruiting date for fruits and seeds) until the time of harvest	M.M^{-1}	mg.kg^{-1}	C or E
R_{sp}	Mass fraction of particles attached to the plant (= rainsplash)	-	-	E

The pollutant concentration in the soil $\overline{C}_{s,t_{exp,veg} \to t_{réc}}$ to be used is the concentration in the surface soil. If the soil layer has not been ploughed, the estimated concentration in the first few centimetres of soil will be taken. For ploughed or dug soil, the average pollutant concentration in the soil over the worked soil depth will be considered. The pollutant concentration in the soil can be estimated from the equations developed in section 1.1.2, with soil depth Z_s differing depending on the case.

Limits associated with using this equation are due to:

- the uncertainty attached to the factor R_{sp}.

  Information sources to define this parameter actually seem to be relatively scarce. The values used to define rainsplash are of the order of a few percent of the dry weight of the plants. Some authors adjust this value depending on the height of the plant;

- estimating the pollutant concentration on soil particles. The pollutant is assumed to have a homogeneous concentration in the mixing zone considered. But, as stated in section 1.1.2.3.6, this assumption is not completely valid. In the case of atmospheric contamination, this assumption may lead to underestimating the concentration of resuspended particles, as the finest particles, once resuspended, are often the most contaminated.

1.6.4.2. USING THE PARTICLE DEPOSITION VELOCITY

This approach is used by several models in the radioecological field (eg. ERMYN, US DOE, 2003; RESRAD, US DOE, 2001; us GENII-S, PNNL, 1988; ECOSYS, Müller et al., 1993).

According to this approach, deposition on the plant ($D_{p\_sol\_p}$) is estimated from the pollutant concentration adsorbed to the particles present in the air and coming from the soil, and the particle deposition velocity.

$$D_{p\_sol\_p} = C_{ap\_sol} \times v_{d\_psol}$$

Equation 1.6.36

Symbol	Parameters	Dimensions	Units	Status
$D_{p\_sol\_p}$	Deposition of pollutant from the soil on plants (after particles are resuspended from the soil)	$M.L^{-2}.T^{-1}$	$m^{-2}.s^{-1}$	C or E
C_{ap_sol}	Pollutant concentration in the air in particulate form coming from the soil (cf. equations 1.2.1 and 1.2.2)	$M.L^{-3}$	$mg.m^{-3}$	C or E
v_{d_psol}	Deposition velocity of resuspended soil particles	$L.T^{-1}$	$m.s^{-1}$	E

The pollutant concentration in plants due to deposition of resuspended soil particles can then be estimated using the same approaches and same equations as presented in section 1.6.2.

To calculate deposition on plants, the pollutant concentration in air C_{ap_sol} used is that at the level of the plants. C_{ap_sol} will be calculated from the pollutant concentration in the surface soil. As in the previous section, the pollutant concentration in the soil may be estimated from the equations developed in section 1.1.2, with soil depth Z_s differing depending on whether or not the soil has been ploughed.

The soil particle deposition velocity depends on a lot of factors, such as particle size, soil roughness and the weather conditions. Depending on these conditions, the literature provides very variable data.

These two parameters, for which specific measurements are rarely available, are sources of uncertainties.

1.6.4.3. COMPARISON OF THE TWO APPROACHES AND ADDITIONAL COMMENTS ON THEIR USE

The US DOE (2003) compared numerical results provided by the ERMYN model (using the approach based on the deposition velocity of particles from the soil) and the BIOMASS model (using the approach based on the mass fraction of particles attached to the plant) for contamination of plants by deposition of particles from the soil. The two models give similar results for vegetables other than leaf vegetables. Conversely, for leaf vegetables, ERMYN gives a concentration one order of magnitude higher than that calculated using BIOMASS. But it is not possible to draw general conclusions about the degree to which one approach overestimates compared to another, because the results cited above depend as much on the assumptions made for the equations (in BIOMASS, adding an assumption about reducing the pollutant concentration in leaf vegetables during preparation, an assumption not made in ERMYN) as on those defined for the parameters. Additional work is required to compare these approaches under identical conditions and with a well-distributed data set.

The results obtained with the equations in sections 1.6.4.1 and 1.6.4.2 generally exhibit significant uncertainties, given the uncertainties attached to the values of parameters used. In the context of an assessment of health risks, if plant contamination by particles from the soil appears to contribute markedly to the exposure of individuals (such as when direct uptake from the soil through the roots is low or very low), it is necessary to compare the results obtained using the two approaches and to discuss the uncertainties associated with estimating the impact of this transfer phenomenon.

However, taking explicit account of this transfer mechanism from the surface

soil to plants using one of the two above approaches assumes that the soil-plant bioconcentration coefficient B_r used in equation 1.6.2 does not already consider possible contamination of the plant by resuspension of particles from the soil (otherwise the impact of this phenomenon would be taken into account twice). So it is advisable to look carefully at the protocol for estimating the coefficient B_r. Indeed, values of B_r estimated from open field culture, in the absence of greenhouses and mulching, *a priori* include the impact of soil particles resuspended by the action of wind and rain.

Some models also refrain from describing this transfer mechanism using specific equations, including its impact by means of the quantity of soil ingested. INERIS does not recommend this last approach, given the scarcity of available data to assign a value to the 'quantity of soil ingested' parameter. As far as we know, there has actually been no study to define a quantity of soil ingested based on the quantity of plant eaten and the growing conditions of these plants (conditions that do or do not promote the resuspension of soil particles).

1.6.5. Concentration in the plant associated with irrigation water

Irrigation water, whatever its type (surface or belowground), can contribute to contaminating plants by pollutant inflow from the soil. Calculating soil deposition by irrigation has been covered in section 1.1.2.2.2 and estimating the expected concentration in the soil from a soil inflow in sections 1.1.2.4 and 1.1.2.5. The contribution of irrigation water to contamination of the plant is therefore included in the calculation of concentration due to direct uptake from the soil (C_{rp}) and in the calculation of the concentration due to deposition of particles from the soil (C_{dsp}).

But irrigation can also be performed by spraying and in this case, in addition to depositing water on the soil, there may also be pollutant on the foliage and fruits. The pollutant concentration due to deposition on the aerial parts of plants by irrigation can be estimated using the same approaches as those developed for particulate deposition from the atmosphere (cf. section 1.6.2).

Deposition by irrigation must be treated as wet deposition. It is therefore necessary to estimate the fraction of wet deposition that adheres to the plants (calculation method from direct deposition on the edible parts: see equation 1.6.7) or the wet capture ratio (calculation method from deposition on the foliage, then taking account of transfer to the edible parts). However it is worth noting that the pollutant can be present in dissolved or particulate form in the water deposited. Depending on the form in which the pollutant is present in the water, there are different data or methods to estimate these parameters.

1.6.6. Comments on not considering secondary transfer phenomena

As stated in section 5 of part A of this document, the calculation approaches developed in this document do not obey the law of conservation of mass, because secondary transfers are not always considered.

In this way, the quantity of pollutant taken up by the plant from the soil is not deducted from the quantity of pollutant present in the soil. If we wished to consider it, we would also have to take account of part of the plants returning to the soil (residues left on site, leaves dropping, etc.).

Nor are the quantities of pollutant deposited on plants deducted from the quantities of pollutant deposited on the soil. Taking them into account would require that the initial fraction not intercepted by plants, plus the quantities lost by plants due to the action of wind and rain are added to the contamination of the soil over time.

Taking these items into account would make the model more complex and in all probability more sensitive to the uncertainties of parameters describing the plant contamination. The choice has been made to take a simplified and conservative approach. This approach is consistent with those used in models for estimating exposures (such as HHRAP, US EPA, 2005; HARP, CalEPA, 2003; CLEA, The Environment Agency, 2002; CSOIL, RIVM, 2007; ERMYN, US DOE, 2003; IAEA, etc.).

1.7. ANIMAL PRODUCTS

To evaluate human exposure, it may be necessary to estimate the contamination:

- of agricultural products (eggs, dairy products, meat),
- products from fishing (fish, shellfish),
- products from hunting (game meat).

As for products of plant origin, the number of animal products for which the concentration has to be modelled depends on the context of the study (exposure pathways for populations, degrees of specificity and precision sought for the study). In the context of a typical agricultural scenario, milk, eggs and meat are often considered. As the exposure conditions of animals are different, a distinction is sometimes made between the pollutant concentration in meat from cattle, pigs, sheep and poultry.

As part of an assessment of environmental risks or environmental monitoring, it may be necessary to estimate pollutant concentrations in other animal species (carnivorous fish, birds, earthworms, etc.).

The pollutant concentration in an animal tissue can be estimated from the concentration in the animal's exposure medium (or media) or from the animal's exposure dose. When the animal's exposure is due to several media (eg. water and food ingested), it is more appropriate to use the animal's exposure dose. But when exposure data for the animals are scarce, it is easier to make the estimate from the concentration in the exposure medium, particularly for animals whose diets are made up from a single food type or from a known biotope.

For animal products from a farm and eaten by man, the most frequent approach is based on the dose, because it takes explicit account of the animals' exposure pathways. For wild animals, the approach based on concentration in the exposure medium is more often used.

In the following sections, the method for calculating the pollutant concentration for domestic animals and wild animals will be treated separately. This formal distinction is based on the amount of information generally available for these two categories of animals. However, there is nothing to prevent the approach presented here for domestic animals being used for wild animals, if the necessary data are available.

Depending on the animals and substances, we sometimes distinguish bioconcentration and bioaccumulation, which are two very similar concepts.

Bioconcentration is the process by which living organisms, particularly those living in water, can extract and concentrate chemical substances from the environment surrounding them. Bioaccumulation also tends to take account of uptake associated with food.

Conversely, there is currently no consensus on the mathematical expressions for the terms 'bioconcentration coefficient' and 'bioaccumulation coefficient'.

In what follows in this document, we will call:

- bioconcentration coefficient: the ratio of the concentration in the animal tissue over the concentration in the animal's exposure medium (water for aquatic organisms, food for other animals);

- biotransfer coefficient: the ratio of the concentration in the animal tissue over the daily exposure dose (or daily exposure dose administered to the animal).

The bioconcentration and bioaccumulation potential of a pollutant by an animal depend on the absorption, distribution and elimination of the pollutant by the organism. For organic substances, this potential generally increases with the hydrophobic nature of substances.

Contaminant absorption by animals causes an increase in the quantity of contaminant in the tissues of these animals until steady state conditions are reached, when the quantity of pollutant absorbed equals the quantity of pollutant degraded or eliminated. The lower the degradation and elimination rates, the longer the time needed to reach steady state conditions and the higher the corresponding concentration in the organism.

In most risk assessments, the pollutant concentrations in animal tissues are calculated under steady state conditions, because pollutant intakes by animals are assumed to be constant over sufficiently long periods that steady state conditions are reached, and the aim is to estimate exposure and chronic risk. In this case, the concentration in products of animal origin is calculated by multiplying the concentration in the exposure medium or the animal's exposure dose by the bioconcentration coefficient or the biotransfer coefficient, respectively.

However, calculations can be performed with a dynamic approach. Such an approach is useful 1) for evaluating concentrations in the tissues before reaching steady state conditions, 2) for estimating the time needed for the concentration to return to the prior level, after a period of high exposure, or 3) if the animal's pollutant intake varies with time.

1.7.1. DOMESTIC ANIMALS

1.7.1.1. ANIMAL EXPOSURE DOSES

The exposure of animals principally takes account of intakes associated with food, water and soil ingested. As part of a risk assessment for man, taking account of the food chain is essentially relevant to non-volatile and semi-volatile substances. For these types of substances, animal exposure by inhalation is low and generally negligible compared to exposure by ingestion.

Food types to be considered depend on the study framework and the animals' living conditions. In a chronic risk assessment (several years' exposure), even if the way the animals are fed varies over the seasons, the quantities of food can be averaged over the year. If conversely, you want to know about the change to concentrations in animal tissues depending on their diet, it will be necessary to define the pollutant, and therefore food, intake based on the seasons.

Exposure by soil ingestion will be based on the pollutant concentration in the surface soil. The bioavailability of a pollutant from the soil may be different to that observed from a foodstuff. Since bioconcentration or biotransfer coefficients are often established from pollutant ingested with foodstuffs, a relative bioavailability coefficient for the soil can be used to take this difference into account (see definition in the glossary).

Hence:

$$D_a = \sum_j \left[Q_{j,a} \times C_j + Q_{s,a} \times C_s \times B_s + Q_{eau,a} \times C_{eau} \right]$$
Equation 1.7.1

Ref: DRC-14-141968-04378A

Symbol	Parameters	Dimensions	Units	Status
D_a	Pollutant quantity to which the animal is exposed per unit time	$M.T^{-1}$	$mg.d^{-1}$	C or E
$Q_{j,a}$	Quantity of matrix j ingested by the animal per unit time	$M.T^{-1}$ or $L^3.T^{-1}$	$kg.d^{-1}$ or $l.d^{-1}$	E
C_j	Pollutant concentration in matrix j	$M.M^{-1}$ or $M.L^{-3}$	$mg.kg^{-1}$ or $mg.l^{-1}$	C or E
C_s	Pollutant concentration in the soil	$M.M^{-1}$	$mg.kg^{-1}$	C or E
$Q_{s,a}$	Mass of soil ingested by the animal per unit time	$M.T^{-1}$	$kg.d^{-1}$	E
B_s	Relative bioavailability coefficient of the pollutant from the soil	-	-	E
C_{eau}	Pollutant concentration in the water	$M.L^{-3}$	$mg.l^{-1}$	C or E
$Q_{eau,a}$	Quantity of water ingested by the animal per unit time	$L^3.T^{-1}$	$l.d^{-1}$	E

Comment: the different matrices ingested by an animal or the matrices ingested by different animals can come from varied exposure zones. In this case, for each matrix, the measured or estimated concentration at the place from which this matrix came should be used. If only the health impact attributable to the site is to be taken into account, the quantities of matrices ingested by the animal that do not come from the site must be subtracted from the total quantities of matrices ingested by the animal.

1.7.1.2. CONCENTRATIONS IN ANIMAL TISSUES

1.7.1.2.1. STEADY STATE APPROACH

The quantity of pollutant to which the animal is exposed is multiplied by the biotransfer coefficient:

$$C_{a,i} = D_a \times B_{T\,a,i}$$ Equation 1.7.2

Symbol	Parameters	Dimensions	Units	Status
$C_{a,\,i}$	Pollutant concentration in tissue i of the animal (i = 1 for meat and i = 2 for eggs and milk)	$M.M^{-1}$ or $M.L^{-3}$	$mg.kg^{-1}$ or $mg.l^{-1}$	C or E
D_a	Pollutant quantity to which the animal is exposed per unit time	$M.T^{-1}$	$mg.d^{-1}$	C or E
$B_{Ta,i}$	Biotransfer coefficient of the pollutant to tissue i of the animal	$T.tissue\ M^{-1}$ or $T.tissue\ L^{-3}$	$d.tissue\ kg^{-1}$ or $d.tissue\ l^{-1}$	C or E

In the absence of the data needed to complete the above equation, the approach based on the concentration present in the exposure medium (or media) and the bioconcentration coefficient is sometimes used.

Hence:

$$C_{a,i} = \frac{\sum_j C_j \times Q_{j,a}}{\sum_j Q_{j,a}} \times BCF_{a,i}$$ Equation 1.7.3

and the biotransfer and bioconcentration coefficients are linked through the following relationship:

$$B_{Ta,i} = \frac{BCF_{a,i}}{\sum_j Q_{j,a}}$$

Equation 1.7.4

Symbol	Parameters	Dimensions	Units	Status
$C_{a,i}$	Pollutant concentration in tissue i of the animal	$M.M^{-1}$ or $M.L^{-3}$	$mg.kg^{-1}$ or $mg.l^{-1}$	C or E
C_j	Pollutant concentration in exposure medium j	$M.M^{-1}$	$mg.kg^{-1}$	C or E
$B_{Ta,i}$	Biotransfer coefficient of the pollutant to tissue i of the animal	$T.tissue$ M^{-1} or $T.tissue$ L^{-3}	$d.tissue$ kg^{-1} or $d.tissue$ l^{-1}	C or E
$BCF_{a,i}$	Bioconcentration coefficient of the pollutant in tissue i of the animal	$Medium$ $M.tissue$ M^{-1} or $Medium$ $M.tissue$ L^{-3}	$Medium$ $kg.tissue$ kg^{-1} or $medium$ $kg.tissue$ l^{-1}	C or E
$Q_{j,a}$	Quantity of medium j ingested by the animal per unit time	$M.T^{-1}$	$kg.d^{-1}$	E

The main difficulty associated with using these relationships comes from defining the biotransfer ($B_{Ta,i}$) or bioconcentration ($BCF_{a,i}$) coefficients.

Thus, care must be taken with the dimensions of the values used for $B_{Ta,i}$ and $BCF_{a,i}$. Depending on the case, these values can be calculated from the pollutant concentration measured in the animal fat, or from the pollutant concentration expressed relative to the dry weight or fresh weight of animal tissue.

Care must also be taken that the conditions under which these parameters were defined were representative of the conditions studied by the user (same exposure level, same type of animal, same exposure matrix and comparable bioavailability of the pollutant). Future documents on the physico-chemical parameters and transfer parameters of chemical substances will show the important criteria for selecting appropriate values for these parameters.

Furthermore, if steady state conditions are not reached, the two ratios 'concentration in animal tissue over animal exposure dose' and 'concentration in animal tissue over average concentration in sampled media' are not constant. As a result, if a previously-unexposed animal experiences an exposure dose (D_1), using equations 1.7.2 or 1.7.3 with a biotransfer or bioconcentration coefficient (estimated under steady state conditions) will lead to overestimating concentrations in animal matrices, as long as steady state conditions are not reached. Conversely, if the exposure dose changes from a value D_1 to a lower value D_2, the concentrations in the animal matrices estimated using this approach will be underestimated so long as new steady state conditions are not reached.

1.7.1.2.2. DYNAMIC APPROACH

1.7.1.2.2.1. CONCENTRATION IN THE ANIMAL'S BODY

Depending on the animal's metabolism, the absorbed substance may be distributed in different tissues and a model with different numbers of

compartments is needed to represent the future outcome of the substance in the animal's body.

Only the simplest case, based on using a single compartment model, is developed here. This compartment then represents all the animal's tissues in which the pollutant is stored and the pollutant concentration in these tissues is assumed to be uniform. Degradation and elimination phenomena are represented by first-order kinetics.

Based on the assumptions described above for the one-compartment model, we can state:

$$\frac{dm_{a,1}}{dt} = t_{abs\,a} \times D_a - k_a \times m_{a,1} - \lambda_a \times m_{a,1}$$
Equation 1.7.5

where $m_{a,1}$: mass of pollutant in the animal's body,

$t_{abs,a}$: absorption rate of the pollutant by the animal,

D_a: pollutant quantity to which the animal is exposed per unit time,

k_a: pollutant elimination coefficient to the milk or eggs by the animal (for cows, ewes, chicken, etc.),

λ_a: pollutant degradation and elimination coefficient by the animal by pathways other than milk or eggs.

1. **If $t_{abs,a}$, D_a, k_a and λ_a are constant,** we can state:

$$m_{a,1}(t) = \frac{t_{abs,a} \times D_a}{k_a + \lambda_a} \times \left(1 - e^{-(k_a + \lambda_a) \times t}\right) + m_{a,1}(0) \times e^{-(k_a + \lambda_a) \times t}$$
Equation 1.7.6

and $\quad C_{a,1}(t) = \frac{t_{abs,a} \times D_a}{(k_a + \lambda_a) \times M_{a,1}(t)} \times \left(1 - e^{-(k_a + \lambda_a) \times t}\right) + \frac{m_{a,1}(0)}{M_{a,1}(t)} \times e^{-(k_a + \lambda_a) \times t}$
Equation 1.

If the mass of pollutant in the animal's body ($m_{a,1}$) is zero at instant 0, we obtain:

$$C_{a,1}(t) = \frac{t_{abs,a} \times D_a}{(k_a + \lambda_a) \times M_{a,1}(t)} \times \left(1 - e^{-(k_a + \lambda_a) \times t}\right)$$
Equation 1.7.8

Symbol	Parameters	Dimensions	Units	Status
$C_{a,1}(t)$	Pollutant concentration at time t in the animal's body	$M.M^{-1}$	$mg.kg^{-1}$	C or E
$M_{a,1}(t)$	Mass of the animal tissues where the pollutant is stored, at time t ($M_{a,1}$ does not include the excreted mass of products such as milk or eggs)	M	kg	E
$m_{a,1}(0)$	Mass of pollutant in the animal's body at instant 0	M	mg	E
λ_a	Pollutant degradation and elimination coefficient by the animal by pathways other than milk or eggs	T^{-1}	d^{-1}	E
k_a	Pollutant elimination coefficient to the milk or eggs by the animal (for cows, ewes, chicken, etc.)	T^{-1}	d^{-1}	E
$t_{abs,a}$	Absorption rate of the pollutant by the animal	-	-	E
D_a	Pollutant quantity to which the animal is exposed per unit time	$M.T^{-1}$	$mg.d^{-1}$	C or E

2. If $t_{abs,a}$, D_a, k_a or λ_a vary over time, $m_{a,1}$ must be integrated over time intervals (Δt) where these parameters can be considered as constant, hence

$$m_{a,1}(t) = \frac{t_{abs,a} \times D_a}{(k_a + \lambda_a)} \times \left(1 - e^{-(k_a + \lambda_a) \times \Delta T}\right) + m_{a,1}(t - \Delta T) \times e^{-(k_a + \lambda_a) \times \Delta T}$$

Equation 1.7.9.

and $$C_{a,1}(t) = \frac{m_{a,1}(t)}{M_{a,1}(t)}$$

Equation 1.7.10

Symbol	Parameters	Dimensions	Units	Status
$m_{a,1}(t)$	Mass of pollutant at time t in the animal's body	M	mg	C or E
$C_{a,1}(t)$	Pollutant concentration at time t in the animal's body	$M.M^{-1}$	$mg.kg^{-1}$	C or E
$M_{a,1}(t)$	Mass of the animal tissues where the pollutant is stored, at time t ($M_{a,1}$ does not include the excreted mass of products such as milk or eggs)	M	kg	E
λ_a	Pollutant degradation and elimination coefficient by the animal by pathways other than milk or eggs	T^{-1}	d^{-1}	E
k_a	Pollutant elimination coefficient to the milk or eggs by the animal (for cows, ewes, chicken, etc.)	T^{-1}	d^{-1}	E
$t_{abs,a}$	Absorption rate of the pollutant by the animal	-	-	E
D_a	Pollutant quantity to which the animal is exposed per unit time	$M.T^{-1}$	$mg.d^{-1}$	C or E

3. **If there is neither degradation nor elimination of the substance by the animal's body,** we can state:

$$C_{a,1}(T) = \frac{\sum_{i=1}^{n} \left[D_a(t_i) \times t_{abs,a}(t_i) \times \Delta t_i \right]}{M_{a,1}(T)}$$

Equation 1.7.11

where i: iteration number between 1 and n,

Ref: DRC-14-141968-04378A

and $\quad \sum_{i=1}^{n} \Delta t_i = T$.

and **if D_a and $t_{abs,a}$ are constant**, we can state:

$$C_{a,1}(T) = \frac{D_a \times T \times t_{abs,a}}{M_{a,1}(T)}$$

Equation 1.7.12

Symbol	Parameters	Dimensions	Units	Status
$C_{a,1}(T)$	Pollutant concentration at time T in the animal's body	M.M^{-1}	mg.kg^{-1}	C or E
$M_{a,1}(T)$	Mass of the animal tissues where the pollutant is stored, at time T ($M_{a,1}$ does not include the excreted mass of products such as milk or eggs)	M	kg	E
$t_{abs,a}$	Absorption rate of the pollutant by the animal	-	-	E
D_a	Pollutant quantity to which the animal is exposed per unit time	M.T^{-1}	mg.d^{-1}	C or E
T	Exposure duration of the animal	T	d	E

Comment: For very lipophilic substances (eg. PCDD, PCDF, PCB), which are almost exclusively stored in animal fat, the approach developed above can be reserved for the fat compartment. In this case, $C_{a,1}$ is the pollutant concentration in animal fat and $M_{a,1}$ is the mass of fat in the animal. The concentration in meat can then be estimated from the pollutant concentration in lipids and the proportion of fat in the meat.

1.7.1.2.2.2. CONCENTRATION IN EXCRETED PRODUCTS (MILK AND EGGS)

The pollutant concentration in excreted products (milk and eggs) can be estimated using the following differential equation:

$$\frac{dm_{a,2}}{dt} = k_a \times m_{a,1}$$

Equation 1.7.13

where $m_{a,2}$: mass of pollutant excreted by the animal,

k_a: elimination coefficient for the substance to the milk or eggs by the animal (for cows, ewes, chicken, etc.),

$m_{a,1}$: mass of pollutant in the animal's body,

or $\quad C_{a,2} \times \dfrac{dM_{a,2}}{dt} + M_{a,2} \times \dfrac{dC_{a,2}}{dt} = k_a \times m_{a,1}$

Equation 1.7.14

where $M_{a,2}$: mass (or volume) of matrix produced by the animal since instant 0,

and $\quad C_{a,2}$: concentration in the matrix (milk or egg) excreted by the animal at time t.

If over the period ΔT considered, concentration variations in the excreted matrix are negligible, we can state:

$$C_{a,2}(\Delta T) = \frac{k_a \times m_{a,1} \times \Delta T}{\Delta M_{a,2}}$$

Equation 1.7.15

where $\Delta M_{a,2}$: variation in mass (or volume) of matric produced by the animal during period ΔT.

If ΔT equals one day, if $t_{abs,a}$, D_a, k_a and λ_a are constant and if the mass (or volume) of matrix produced per day by the animal is constant and equals $M^j_{a,2}$, then the average concentration at day j in the excreted matrix is given by:

$$C_{a,2,moy\_j} = \frac{k_a \times m_{a,1}(t)}{M^j_{a,2}}$$

Equation 1.7.16

If $t_{abs,a}$, D_a, k_a and λ_a are constant, we can state:

$$C_{a,2,moy\_j} = \frac{k_a}{k_a + \lambda_a} \cdot \frac{t_{abs,a} \times D_a}{M^j_{a,2}} + \frac{k_a}{M^j_{a,2}} \cdot \left[m_{a,1}(0) - \frac{t_{abs,a} \times D_a}{(k_a + \lambda_a)} \right] \times e^{-(k_a + \lambda_a) \times t}$$

Equation 1.7.17

Symbol	Parameters	Dimensions	Units	Status
$C_{a,2,moy\_j}$	Average pollutant concentration in the matrix (milk or egg) excreted by the animal at day j	M.M^{-1} or M.L^{-3}	mg.kg^{-1} or mg.l^{-1}	C or E
$m_{a,1}(t)$	Mass of pollutant in the animal's body at day j	M	mg	E
λ_a	Pollutant degradation and elimination coefficient by the animal by pathways other than milk or eggs	T^{-1}	d^{-1}	E
k_a	Pollutant elimination coefficient to the milk or eggs by the animal (for cows, ewes, chicken, etc.)	T^{-1}	d^{-1}	E
$t_{abs,a}$	Absorption rate of the pollutant by the animal	-	-	E
D_a	Pollutant quantity to which the animal is exposed per day	M.T^{-1}	mg.d^{-1}	C or E
$m_{a,1}(0)$	Mass of pollutant in the animal's body at instant 0	M	mg	E
$M^j_{a,2}$	Mass or volume of matrix produced per day by the animal	M.T^{-1}	kg.d^{-1} or l.d^{-1}	E

1.7.1.2.3. TIME NEEDED TO REACH STEADY STATE CONDITIONS AND ESTIMATE OF TRANSFER COEFFICIENTS

When $M_{a,1}$ is constant, it can be considered that $C_{a,1}$ is close to steady state conditions if:

$$C_{a,1} \approx \frac{t_{abs,a} \times D_a}{(k_a + \lambda_a) \times M_{a,1}}$$

Equation 1.7.18

or if $\quad e^{-(k_a + \lambda_a)t} \to 0$

Equation 1.7.19

(cf. equation 1.7.8)

Hence, when $t \geq \dfrac{3}{k_a + \lambda_a}$,

$$e^{-(k_a + \lambda_a)t} < 0,05$$

Equation 1.7.20

As a result, if animals are exposed to a constant quantity of pollutant (D_a) over time, beyond an exposure duration of $\dfrac{3}{k_a + \lambda_a}$, the approach based on transfer coefficients and steady state conditions gives results similar to the dynamic approach.

According to equations 1.7.2 and 1.7.18, we can therefore state:

$$B_{Ta,1} = \frac{t_{abs,a}}{(k_a + \lambda_a) \times M_{a,1}}$$

Equation 1.7.21

Symbol	Parameters	Dimensions	Units	Status
$B_{Ta,1}$	Biotransfer coefficient in the animal's body	T.tissue M^{-1}	d.tissue kg^{-1}	C or E
$M_{a,1}$	Mass of the animal tissues where the pollutant is stored, ($M_{a,1}$ does not include the excreted mass of products such as milk or eggs)	M	kg	E
λ_a	Pollutant degradation and elimination coefficient by the animal by pathways other than milk or eggs	T^{-1}	d^{-1}	E
k_a	Pollutant elimination coefficient to the milk or eggs by the animal (for cows, ewes, chicken, etc.)	T^{-1}	d^{-1}	E
$t_{abs,a}$	Absorption rate of the pollutant by the animal	-	-	E

Comment: if the pollutant is stored mainly in fat tissues and $B_{Ta,1}$ is the transfer coefficient in animal fat, the transfer coefficient in meat is calculated by multiplying equation 1.7.21 by the proportion of fat in the meat.

The expression for biotransfer coefficient in excreted products (milk and eggs) can be deduced from equation 1.7.14. According to this equation, we can state:

$$\frac{dC_{a,2}}{dt} = \frac{k_a \times M_{a,1} \times C_{a,1}}{M_{a,2}} - C_{a,2} \times \frac{1}{M_{a,2}} \times \frac{dM_{a,2}}{dt}$$

Equation 1.7.22

If $M_{a,1}$ is constant and $M_{a,2}(t) = M_{a,2}^{j} \times t$,

then $\dfrac{dC_{a,2}}{dt} = \dfrac{k_a \times M_{a,1} \times C_{a,1}}{M^j_{a,2} \times t} - \dfrac{C_{a,2}}{t}$

Equation 1.7.23

Under steady state conditions, we obtain:

$$C_{a,2} = \dfrac{k_a \times M_{a,1} \times C_{a,1}}{M^j_{a,2}}$$

Equation 1.7.24

and according to equations 1.7.2 and 1.7.18, we can therefore state:

$$B_{Ta,2} = \dfrac{k_a}{k_a + \lambda_a} \times \dfrac{t_{abs,a}}{M^j_{a,2}}$$

Equation 1.7.25

Symbol	Parameters	Dimensions	Units	Status
$B_{Ta,2}$	Biotransfer coefficient in products (milk and egg) excreted by the animal	T.tissue M^{-1} or T.tissue L^{-3}	d.tissue kg^{-1} or d.tissue l^{-1}	C or E
$M^j_{a,2}$	Mass or volume of matrix produced per day by the animal	$M.T^{-1}$ or $L^3.d^{-1}$	$kg.d^{-1}$ or $l.d^{-1}$	E
λ_a	Pollutant degradation and elimination coefficient by the animal by pathways other than milk or eggs	T^{-1}	d^{-1}	E
k_a	Pollutant elimination coefficient to the milk or eggs by the animal (for cows, ewes, chicken, etc.)	T^{-1}	d^{-1}	E
$t_{abs,a}$	Absorption rate of the pollutant by the animal	-	-	E

Comments:

1. If the absorption rate is not known, it can be taken as 1, as a first approach, which assumes total absorption of the pollutant from foodstuffs and water ingested, and is therefore a conservative approach.

2. If λ_a equals 0, the equations for calculating concentrations in animal tissues are simplified.
   Thus,

$$B_{Ta,1} = \dfrac{t_{abs,a}}{k_a \times M_{a,1}}$$

Equation 1.7.26

and $\quad B_{Ta,2} = \dfrac{t_{abs,a}}{M^j_{a,2}}$

Equation 1.7.27

3. The equations presented in section 1.7.1.2.2 to estimate concentrations in the animal's body and excreted products using a dynamic approach are based on the animal's exposure dose. Equations of the same type can be written using the concentration in the exposure medium (or media) (cf. section 1.7.2.2).

In fact, equation 1.7.5 can be replaced by:

$$\frac{dm_{a,1}}{dt} = t_{abs,a} \times Q_a \times \overline{C}_{j,a} - k_a m_{a,1} - \lambda_a m_{a,1}$$

Equation 1.7.28

where $m_{a,1}$: mass of pollutant in the animal's body,

$t_{abs,a}$: pollutant absorption rate by the animal,

k_a: pollutant elimination coefficient to the milk or eggs by the animal (for cows, ewes, chicken, etc.),

λ_a: pollutant degradation and elimination coefficient by the animal by pathways other than milk or eggs,

Q_a: total quantity of matrix (matrices) ingested by the animal per day ($= \sum_j Q_{j,a}$),

$\overline{C}_{j,a}$: weighted average of pollutant concentrations in the matrix (matrices) ingested by the

animal ($\overline{C}_{j,a} = \dfrac{\sum_j C_j \times Q_{j,a}}{\sum_j Q_{j,a}}$),

hence $\dfrac{dm_{a,1}}{dt} = K_{abs,a} \times \overline{C}_{j,a} - k_a m_{a,1} - \lambda_a m_{a,1}$

Equation 1.7.29

where $\mathrm{K}_{abs,a} = \mathrm{t}_{abs,a} \times Q_a$

Equation 1.7.30

The resulting expressions for $C_{a,1}$ and $C_{a,2}$ are identical to those developed above, with $K_{abs,a} \times \overline{C}_{j,a}$ replacing $t_{abs\,a} \times D_a$.

1.7.2. WILD ANIMALS

The pollutant concentration in the animal's body is calculated from the concentration in the animal's exposure medium (or from the average concentration in the exposure media).

As before, it can be estimated using a steady-state or dynamic approach.

1.7.2.1. STEADY STATE APPROACH

$$C_a = C_{me} \times BCF_a$$

Equation 1.7.31

Symbol	Parameters	Dimensions	Units	Status
C_a	Pollutant concentration in the animal's body	M.M^{-1}	mg.kg^{-1}	C or E
BCF_a	Bioconcentration coefficient in the animal's body	Medium M.tissue M^{-1} or Medium L.tissue M^{-1}	Medium kg.tissue kg^{-1} or medium m^3.tissue kg^{-1}	C or E
C_{me}	Concentration in the animal's exposure medium or media	M.M^{-1} or M.L^{-3}	mg.kg^{-1} or mg.m^{-3}	C or E

<u>Comments:</u>

1. For fish, the exposure medium is water. However, depending on the data sources, the bioconcentration coefficient is defined relative to the pollutant concentration in dissolved form or relative to the pollutant concentration in the water in particulate and dissolved forms. It is therefore important that the concentration used is consistent with the definition of the bioconcentration coefficient. In certain cases, a bioconcentration coefficient may also have been defined relative to the concentration in sediments (we refer in preference to a bioaccumulation coefficient) and the concentration to be used is therefore that in the sediments.

2. For certain substances, pollutant concentrations in predator organisms are higher than in the organisms these predators consume (relative to the fat content). This is then called bioamplification and we may then have to estimate pollutant concentrations throughout the trophic chain.

   Under steady state conditions, we can state:

$$C_{pred} = C_{proie} \times BCF_{pred}$$

Equation 1.7.32

where C_{pred}: pollutant concentration in the predator animal,

BCF_{pred}: bioconcentration coefficient relating to the predator,

C_{proie}: pollutant concentration in the prey,

$$C_{proie} = C_{me} \times BCF_{proie}$$

hence $C_{pred} = C_{me} \times BCF_{proie} \times BCF_{pred}$

Equation 1.7.33

BCF_{pred} is sometimes called the biomagnification coefficient (English alternative to bioamplification).

1.7.2.2. DYNAMIC APPROACH

As before, the approach consists of representing the animal using a single compartment and the differential equation expresses exchanges between the exposure medium and the animal over time.

$$\frac{dm_a}{dt} = k_{1,a} \times V_{me} \times C_{me} - k_{2,a} m_a - \lambda'_a m_a$$

Equation 1.7.34

where m_a: mass of pollutant in the animal's body,

$k_{1,a}$: absorption rate of pollutant by the animal's body,

V_{me}: volume of the exposure medium,

C_{me}: concentration in the exposure medium,

$k_{2,a}$: elimination coefficient for the pollutant by the animal's body,

λ'_a: degradation coefficient of pollutant by the animal's body.

Comment: In the case of fish, the exposure medium is surface water and $k_{2,a} \times m_a$ is the quantity of pollutant discharged into the water per unit time by the fish. If the quantity of pollutant in the water is much greater than the quantity of pollutant in the fish, we can consider that C_{me} is not modified by $k_{2,a} \times m_a$.

1. **If C_{me}, $k_{1,a}$, $k_{2,a}$ and λ'_a are constant,** we can state:

$$m_a(t) = \frac{k_{1,a} \times V_{me} \times C_{me}}{k_{2,a} + \lambda'_a} \times \left(1 - e^{-(k_{2,a}+\lambda'_a)\times t}\right) + m_a(0) \times e^{-(k_{2,a}+\lambda'_a)\times t}$$

Equation 1.7.35

And $$C_a(t) = \frac{K_{1,a} \times C_{me}}{(k_{2,a} + \lambda'_a) \times M_a(t)} \times \left(1 - e^{-(k_a+\lambda'_a)\times t}\right) + \frac{m_a(0) \times e^{-(k_{2,a}+\lambda'_a)\times t}}{M_a(t)}$$

Equation 1.7.36

where $K_{1,a} = k_{1,a} \times V_{me}$

Equation 1.7.37

The mass of the animal's body (M_a) is often considered as constant over time. Furthermore, if the mass of pollutant in the animal's body (m_a) is zero at instant 0, then it is possible to state:

$$C_a(t) = \frac{K_{1,a} \times C_{me}}{(k_{2,a} + \lambda'_a) \times M_a} \times \left(1 - e^{-(k_{2,a}+\lambda'_a)\times t}\right)$$

Equation 1.7.38

or $$C_a(t) = \frac{K_{1,a}}{K_{2,a}} \times C_{me} \times \left(1 - e^{-(k_{2,a}+\lambda'_a)\times t}\right)$$

Equation 1.7.39

where $K_{2,a} = (k_{2,a} + \lambda'_a) \times M_a$

Equation 1.7.40

Symbol	Parameters	Dimensions	Units	Status
$C_a(t)$	Pollutant concentration in the animal's body at time t	M.M^{-1}	mg.kg^{-1}	C or E
C_{me}	Pollutant concentration in the exposure medium	M.L^{-3}	mg.m^{-3}	C or E
$K_{1,a}$	Mass transfer coefficient from the exposure medium to the animal's body	Medium L^3. T^{-1}	Medium m^3.d^{-1}	E
$K_{2,a}$	Mass transfer coefficient from the animal's body to the exposure medium	Tissue M.T^{-1}	Tissue kg.d^{-1}	E

Comment: under steady state conditions, the concentration in the animal's body (C_a) is constant and we can state:

$$C_a = \frac{K_{1,a}}{K_{2,a}} \times C_{me}$$

Equation 1.7.41

From this we deduce,

$$BCF_a = \frac{K_{1,a}}{K_{2,a}}$$

Equation 1.7.42

2. If C_{me}, $k_{1,a}$, $k_{2,a}$ or λ'_a vary over time, equation 1.7.34 must be integrated over time intervals (ΔT) where these parameters can be considered constant:

hence $m_a(t) = \frac{K_{1,a} \times C_{me}}{(k_{2,a} + \lambda'_a)} \times \left(1 - e^{-(k_{2,a} + \lambda'_a) \times \Delta T}\right) + m_a(t - \Delta T) \times e^{-(k_{2,a} + \lambda'_a) \times \Delta T}$

Equation 1.7.43.

and $C_a(t) = \frac{K_{1,a}}{K_{2,a}} \times C_{me} \times \left(1 - e^{-(k_{2,a} + \lambda'_a) \times \Delta T}\right) + \frac{m_a(t - \Delta T)}{M_a(t)} \times e^{-(k_{2,a} + \lambda'_a) \times \Delta T}$

Equation 1.7.44

Symbol	Parameters	Dimensions	Units	Status
C_a (t)	Pollutant concentration in the animal's body at time t	M.M^{-1}	mg.kg^{-1}	C or E
m_a (t)	Mass of pollutant in the animal's body at time t	M	mg	C or E
M_a (t)	Mass of the animal's body at time t	M	kg	E
C_{me}	Pollutant concentration in the exposure medium	M.L^{-3}	mg.m^{-3}	C or E
$K_{1,a}$	Mass transfer coefficient from the exposure medium to the animal's body	Medium L^3. T^{-1}	Medium m^3.d^{-1}	E
$K_{2,a}$	Mass transfer coefficient from the animal's body to the exposure medium	Tissue M.T^{-1}	Tissue kg.d^{-1}	E

2. ESTIMATION OF EXPOSURE LEVELS

Calculations of exposure levels by:

- respiratory pathways,
- oral pathways,
- dermal pathways,

are presented one after the other.

To calculate sub-chronic and chronic risks, it is necessary to calculate average exposure levels over durations extending from a few days to several years. These average exposure levels must be calculated as the average of exposure levels over the exposure period. As stated in section 1.1.2, an average external exposure dose for a given duration can sometimes also be estimated from average concentrations in exposure media, if these concentrations can be calculated easily using an analytical expression and if the exposure parameters of the receptor can be considered as constant over this period (cf. sections 2.2 and 2.3.2).

2.1. EXPOSURE BY INHALATION

The concentration inhaled (C_{inh}) is calculated as the sum of the pollutant concentration in gaseous form (C_{ag}) and the pollutant concentration in inhalable particulate form (C_{ap_inh}):

$$C_{inh} = C_{ag} + C_{ap\_inh}$$

Equation 2.1.1

C_{ap_inh} is generally compared to the pollutant concentration adsorbed to particles with diameters less than or equal to 10 μm (cf. section 1.2.1).

The average inhaled pollutant concentration is calculated as the sum of concentrations in different places ('outdoor areas and/or indoor areas'), visited during the exposure period, weighted by the time fraction spent in each place.

The average inhaled concentration over the exposure period (d_{exp}) from T_1 to T_2 is therefore given by:

$$\overline{C_{inh}}(d_{exp}) = \frac{\sum_{i=1}^{n} C_{inh}(t_i) \times \Delta t_i}{T_2 - T_1}$$

Equation 2.1.2

where Δt_i: period during which the inhaled concentration equals $C_{inh}(t_i)$,

$$\sum_{i=1}^{n} \Delta t_i = T_2 - T_1$$

n: number of time increments,

i: iteration number between 1 and n.

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Symbol	Parameters	Dimensions	Units	Status
$\overline{C_{inh}}(d_{exp})$	Average concentration inhaled over the exposure period d_{exp}	M.L^{-3}	mg.m^{-3}	C or E
$C_{inh}(t_i)$	Concentration inhaled at time t_i	M.L^{-3}	mg.m^{-3}	C or E
Δt_i	Period during which the inhaled concentration equals $C_{inh}(t_i)$	T	d	E
C_{ap_inh}	Pollutant concentration in the air in inhalable particulate form	M.L^{-3}	mg.m^{-3}	C or E
C_{ag}	Pollutant concentration in the air in gaseous form	M.L^{-3}	mg.m^{-3}	C or E
d_{exp}	Duration of the exposure period considered: $d_{exp} = T_2 - T_1$	T	d	C or E
T_1	Beginning of the exposure period	T	d	E
T_2	End of the exposure period	T	d	E

2.2. EXPOSURE BY SOIL INGESTION

The exposure dose by soil ingestion (E_s) is given by:

$$E_s = \frac{Q_{s\_p} \times C_{s,ing} \times B_s}{B_w}$$

Equation 2.2.1

where $C_{s,ing}$: pollutant concentration in the ingested soil or in the soil fraction of ingested dust,

B_s: relative bioavailability coefficient of the pollutant in the soil (compared to the bioavailability of pollutant in the matrix used to determine the toxicological reference value),

B_w: body mass of the receptor,

Q_{s_p}: quantity of soil and dust (weighted by the soil fraction in the dust) ingested:

$$Q_{s\_p} = Q_s + Q_{pous} \times f_{s\_pous}$$

Equation 2.2.2

where Q_s: quantity of soil ingested,

Q_{pous}: quantity of dust ingested,

and f_{s_pous}: soil fraction in the dust.

Comments:

1. Given the quality of data available to estimate soil and dust quantities ingested, it is difficult to distinguish soil quantities ingested through exterior soil and through dust.

2. $C_{s,ing}$ is generally defined as the pollutant concentration in the surface soil. Since soil particles adhering to the fingers are the finest particles, this fraction can have a different concentration, often higher than in the soil *in situ*. The assessor can therefore define the concentration in the ingested soil as the concentration measured in this fraction (US EPA (1994), in the user guide for the IEUBK model, recommends using the concentration measured in the fraction smaller than 250 µm) or weight the concentration modelled in the surface layer by an enrichment factor. But the definition of this value for this parameter can also be a source of uncertainties.

3. As Q_{s_p} is generally defined on the basis of a soil mass ingested per day, $C_{s,ing}$ can then be estimated from the average of concentrations in soils in the places visited by the receptor during one day, taking account of the time fraction spent in each place and the type of activities carried out in these places (activities that do or do not promote contact with the soil).

4. The bioavailability of the pollutant from the soil may be different (it is often less) from that observed when the pollutant is diluted in water or ingested with foodstuffs. To take account of the difference in bioavailability between the pollutant ingested with soil and that for the pollutant on the matrix used to establish the toxicological reference value, a relative bioavailability coefficient can be used. But little data are available as yet to define this parameter. Work (Caboche, 2009) has shown the possibility of estimating the relative bioavailability of certain pollutants in soil from the bioaccessibility of these pollutants measured using *in vitro* methods (INERIS, 2010). But in the absence of data, a default, over-estimating value of 1 is generally assigned to the coefficient B_s.

Over the exposure period (d_{exp}) lasting from T_1 to T_2, the average exposure dose by soil ingestion is calculated as the average of pollutant doses ingested from the soil from T_1 to T_2. If d_{exp} is broken up into n sub-periods each of duration Δt_i, for which the exposure dose $E_s(t_i)$ can be considered constant, then:

$$\overline{E_s}(d_{exp}) = \frac{\sum_{i=1}^{n} E_s(t_i) \times \Delta t_i}{T_2 - T_1}$$

Equation 2.2.3

where i: iteration number (number of the sub-period considered) between 1 and n,

and $\quad \sum_{i=1}^{n} \Delta t_i = T_2 - T_1$

Symbol	Parameters	Dimensions	Units	Status
$\overline{E_s}(d_{exp})$	Average exposure dose by soil ingestion over the exposure period d_{exp}	M.M^{-1}.T^{-1}	mg.kg^{-1}.d^{-1}	C
$E_s(t_i)$	Exposure dose by soil ingestion at time t_i	M.M^{-1}.T^{-1}	mg.kg^{-1}.d^{-1}	C
Δt_i	Period during which the exposure dose equals $E_s(t_i)$	T	d	E
$C_{s,ing}$	Pollutant concentration in the ingested soil	M.M^{-1}	mg.kg^{-1}	C or E
Q_{s_pous}	Mass of soil and dust (mass of dust expressed relative to the concentration in the soil) ingested per unit time	M.T^{-1}	kg.d^{-1}	C or E
Q_s	Mass of soil ingested per unit time	M.T^{-1}	kg.d^{-1}	E
Q_{pous}	Mass of interior dust ingested per unit time	M.T^{-1}	kg.d^{-1}	E
f_{s_pous}	Soil fraction in the dust	-	-	E
d_{exp}	Duration of the exposure period considered: d_{exp} = T_2-T_1	T	d	C or E
T_1	Beginning of the exposure period	T	d	E
T_2	End of the exposure period	T	d	E
B_w	Body mass of the receptor	M	kg	E
B_s	Relative bioavailability coefficient of the pollutant in the soil (compared to the bioavailability of pollutant in the matrix used to determine the toxicological reference value)	-	-	E

Comment: if Q_{s_p}, B_s and B_w can be considered as constant over the exposure period d_{exp}, the average exposure dose by soil ingestion over this period can also be written:

$$\overline{E_s}(d_{exp}) = \frac{\overline{C_{s,ing}}(d_{exp}) \times Q_{s\_p} \times B_s}{B_w}$$

Equation 2.2.4

where $\overline{C_{s,ing}}(d_{exp})$: average pollutant concentration in the ingested soil (cf. section 1.1.2.5) and in the soil fraction of ingested dust during the period d_{exp}.

2.3. EXPOSITION BY INGESTION OF FOODSTUFFS

2.3.1. CALCULATION OF CONCENTRATIONS IN PRODUCTS OF PLANT AND ANIMAL ORIGIN CONSUMED BY MAN

1. On a farm, consumed products of animal origin come from different animals making up a herd or flock. These different individuals may have been exposed over diff periods from concentrations in different media. Depending on the study requirements, the assessor may need to estimate the average or maximum concentration at a given instant in the animal matrices within the herd or flock.

2. The calculation methods presented in sections 1.6 and 1.7 are for concentrations in products before preparation. The preparation of food from raw products can, depending on the situation, reduce or increase the pollutant concentration of the product consumed compared to the raw product.

Thus, washing and peeling tend to reduce the pollutant concentration in products. In this case, a 'decontamination coefficient' ($f_{déc}$) can be used to take account of this reduction of the concentration in the product actually consumed (C_{prod_cons}) compared to the concentration in the raw product (C_{brut}).

$$C_{prod\_cons} = C_{brut} \times f_{déc}$$

Equation 2.3.1

$f_{déc}$ is between 0 and 1. A conservative approach is very often selected and $f_{déc}$ is assumed to be 1.

Conversely, certain food products can be prepared by concentrating a base product.

For example, cheese or butter made from milk have a much high fat concentration than the milk. For very lipophilic pollutants, the pollutant concentration in the cheese or butter will be much higher than in the milk. For these pollutants, the exposure dose associated with dairy products should be estimated:

- either from the pollutant concentration in the fat and the sum of fat quantities consumed in different milk-based products,

- or from the pollutant concentration of different dairy products multiplied by the quantities consumed expressed in fresh weight for each product. In this case, the pollutant concentration in the dairy product considered can be estimated from the concentration in the milk and the ratio of fat content between the two products.

$$C_{prod\_lacté} = C_{lait} \times \frac{t_{lip\_prod\_lacté}}{t_{lip\_lait}}$$

Equation 2.3.2

where $C_{prod\_lacté}$: concentration of lipophilic pollutant in the dairy product, expressed as fresh weight,

C_{lait}: concentration of lipophilic pollutant in the milk, expressed as fresh weight,

$t_{lip\_prod\_lacté}$: lipid content in the dairy product,

t_{lip_lait}: lipid content in the milk.

2.3.2. CALCULATING THE EXPOSURE DOSE ASSOCIATED WITH INGESTION OF FOODSTUFFS

To evaluate risks due contamination of the site, only the fraction of foodstuffs from the zone affected by the site studied should be considered.

The exposure dose by ingestion of food (including water if the water source used for human consumption is affected by the contamination of the site studied) is given by:

$$E_{prod\_cons} = \frac{\sum_j Q_{prod\_cons,j} \times C_{prod\_cons,j} \times f_{prod\_cons\_exp,j}}{B_w}$$

Equation 2.3.3

where $Q_{prod\_cons,j}$: quantity of food product j consumed by the receptor,

$C_{prod\_cons,j}$: pollutant concentration in food j,

$f_{prod\_cons\_exp,j}$: fraction of food quantity j consumed and exposed to the contamination of the site,

B_w: body mass of the receptor.

Comment:

The exposure dose associated with ingestion of food products affected by the site is expressed as a function of the quantities of foodstuffs ingested. It should be emphasised that, depending on the studies, the protocols used to estimate the quantities of food consumed by individuals vary. In some cases estimates may be based on purchases. Since the quantities actually ingested are smaller, an additional loss factor can be introduced where appropriate.

Over the exposure period (d_{exp}) lasting from T_1 to T_2, the average exposure dose by ingestion of foodstuffs is calculated as the average of pollutant doses ingested from the foodstuffs from T_1 to T_2. If d_{exp} is broken up into n sub-periods each of duration Δt_i, for which the exposure dose E_{prod_cons} (t_i) can be considered constant, then:

$$\overline{E_{prod\_cons}}(d_{exp}) = \frac{\sum_{i=1}^{n} E_{prod\_cons}(t_i) \times \Delta t_i}{T_2 - T_1}$$

Equation 2.3.4

where i: iteration number (number of the sub-period considered) between 1 and n,

and $\quad \sum_{i=1}^{n} \Delta t_i = T_2 - T_1$

Symbol	Parameters	Dimensions	Units	Status
$\overline{E_{prod\_cons}}(d_{\exp})$	Average exposure dose by ingestion of foodstuffs over the exposure period $d_{\exp}$	M.M^{-1}.T^{-1}	mg.kg^{-1}.d^{-1}	C
$E_{prod\_cons}(t_i)$	Exposure dose by ingestion of foodstuffs at time t_i	M.M^{-1}.T^{-1}	mg.kg^{-1}.d^{-1}	C
Δt_i	Period during which the exposure dose equals $E_{prod\_cons}(t_i)$	T	d	E
$Q_{prod\_cons,j}$	Quantity of food product j consumed by the receptor	M.T^{-1}	kg.d^{-1}	E
$C_{prod\_cons,j}$	Pollutant concentration in foodstuff j	M.M^{-1}	mg.kg^{-1}	C or E
$f_{prod\_cons\_exp,j}$	Fraction of food quantity j consumed and exposed to the contamination of the site	-	-	E
$d_{\exp}$	Duration of the exposure period considered: $d_{\exp} = T_2-T_1$	T	d	C or E
T_1	Beginning of the exposure period	T	d	E
T_2	End of the exposure period	T	d	E
B_w	Body mass of the receptor	M	kg	E

Comment: If $Q_{prod\_cons,j}$, $f_{prod\_cons\_exp,j}$ and B_w can be considered as constant over the exposure period $d_{\exp}$, the average exposure dose by ingestion of plant and animal foodstuffs over this period can also be written:

$$\overline{E_{prod\_cons}}(d_{\exp}) = \frac{\sum_{j} Q_{prod\_cons,j} \times \overline{C_{prod\_cons,j}}(d_{\exp}) \times f_{prod\_cons\_exp,j}}{B_w} \qquad \text{Equation 2.3.5}$$

where $Q_{prod\_cons,j}$: quantity of food product j consumed,

$\overline{C_{prod\_cons,j}}(d_{\exp})$: average pollutant concentration in foodstuff j during period $d_{\exp}$ (for plants, the concentrations are again the concentrations after harvest, of course).

2.4. Exposure of babies by ingestion of breast milk

The exposure of a baby is estimated from the contamination level in the breast milk.

2.4.1. Concentration in breast milk

A great many pollutants have been found in breast milk (US EPA, 1998):

- very lipophilic pollutants (such as polychlorodibenzodioxins and polychlorodibenzofurans, etc.), which are almost exclusively in the lipid phase of the milk,
- substances with lower octanol-water partition coefficients (such as phenols, certain aldehydes, etc.), present in both the lipid and aqueous phases of the milk,
- inorganic compounds and organo-metallic substances. Metallic substances are generally present in the aqueous phase and bound to proteins, peptides or amino acids. Certain organo-metallic substances and certain metalloids can be present in both the lipid and aqueous phases.

In the same way as for products of animal origin, modelling pollutant concentrations in breast milk will be presented using simple approaches. Multi-compartmental models taking account of the distribution and transfer of pollutants between different tissues (pharmacokinetic models) go beyond the scope of this document. These models as used to estimate pollutant concentrations in the mother's different tissues and milk over time. But the compartments considered depend on the substance studied and numerous specific parameters are needed for each substance. For more information about these models, the reader should refer to publications such as Verner et al. (2009), who produced and tested a pharmacokinetic model for persistent organic pollutants.

2.4.1.1. Estimate based on the transfer coefficient

In the same way as for products of animal origin, the pollutant concentration in milk is sometimes estimated from the mother's exposure and a biotransfer coefficient:

$$C_{lait\_mat} = D_m \times B_{T\_lait\_mat}$$

Equation 2.4.1

Symbol	Parameters	Dimensions	Units	Status
C_{lait_mat}	Pollutant concentration in the breast milk	M.M^{-1}	mg.kg^{-1}	C or E
D_m	Quantity of pollutant to which the mother is exposed per day (daily external exposure dose multiplied by the mother's body mass)	M.T^{-1}	mg.d^{-1}	C or E
$B_{T\ lait\_mat}$	Biotransfer coefficient of the pollutant to the breast milk	T.milk M^{-1}	d.milk kg^{-1}	C or E

Comment: for very lipophilic substances, the biotransfer coefficient can be related to the lipid fraction of the milk and the concentration in the milk can be calculated by multiplying the pollutant concentration in the lipid phase by the fat content of the breast milk.

Depending on the available data, two approaches can be used to estimate concentrations in breast milk over time.

The first is identical to that used for milk and eggs produced by animals. It assumes that the rate of pollutant elimination or transfer to the breast milk is known. The second, from US EPA (1998), consists of calculating firstly the concentration in the lipid phase of the milk and secondly the concentration in the aqueous phase. This approach assumes that the pollutant concentration in the lipid fraction of the milk equals the pollutant concentration in the mother's fatty tissues.

2.4.1.2.1. FOR CASES WHERE THE ELIMINATION CONSTANT IN BREAST MILK IS KNOWN

The pollutant mass balance in the mother is described by the following differential equation:

$$\frac{dm_m}{dt} = t_{abs,m} \times D_m - k_p \times m_m$$

Equation 2.4.2

where m_m: mass of pollutant in the mother's body,

D_m: quantity of pollutant to which the mother is exposed per day (daily external exposure dose multiplied by the mother's body mass),

k_p: loss coefficient from the mother's body (degradation and/or excretion),

$t_{abs,m}$: pollutant absorption rate by the mother.

1. **If $t_{abs,m}$, D_m and k_p are constant,** integrating this equation leads to:

$$m_m(t) = \frac{t_{abs,m} \times D_m}{k_p} \times \left(1 - e^{-k_p \times t}\right) + m_m(0) \times e^{-k_p \times t}$$

Equation 2.4.3

where $m_m(0)$: mass of pollutant in the mother's body at t=0.

2. If $t_{abs,m}$, D_m or k_p vary over time, m_m must be integrated over time intervals (Δt) where these parameters can be considered as constant:

hence $$m_m = \frac{t_{abs,m} \times D_m}{k_p} \times \left(1 - e^{-k_p \times \Delta t}\right) + m_m(t - \Delta t) \times e^{-k_p \times \Delta t}$$

Equation 2.4.4

The loss coefficient (k_p) varies over the course of the woman's life.

- **Before the breast-feeding period (t < $t_{pré\_all}$),**

$$k_p = k_{pré\_all}$$

As a result, **if $t_{abs,m}$, D_m and k_p are constant before breast-feeding,** the mass of pollutant in the mother's body at the moment breast-feeding begins equals:

$$m_m(t_{pré\_all}) = \frac{t_{abs,m} \times D_m}{k_{pré\_all}} \times \left(1 - e^{-k_{pré\_all} \times t_{pré\_all}}\right) + m_m(0) \times e^{-k_{pré\_all} \times t_{pre\_all}}$$

Equation 2.4.5

where $t_{pré\_all}$: breast-feeding start date,

and taking a sufficiently large value $t_{pré\_all}$, we can state:

$$m_m(t_{pré\_all}) \approx \frac{t_{abs,m} \times D_m}{k_{pré\_all}} \times \left(1 - e^{-k_{pré\_all} \times t_{pre\_all}}\right)$$

Equation 2.4.6

- **During the breast-feeding period,** excretion of milk is expressed as an additional pollutant loss.

  The loss coefficient (k_p) then equals:

$$k_p = k_{pré\_all} + k_{all}$$

Equation 2.4.7

where k_{all}: pollutant elimination coefficient to breast milk.

For t > $t_{pré\_all}$, **if $t_{abs,m}$, D_m, $k_{pré\_all}$ and k_{all} are constant**, then:

$$m_m(t) = m_m(t_{pré\_all}) \times e^{-(k_{pré\_all} + k_{all}) \times (t - t_{pré\_all})} + \frac{t_{abs,m} \times D_m}{k_{pré\_all} + k_{all}} \times \left(1 - e^{-(k_{pré\_all} + k_{all}) \times (t - t_{pré\_all})}\right)$$

Equation 2.4.8

and **if the quantity of pollutant to which the mother is exposed per day is the same before and after the start of breast-feeding,** we can state:

$$m_m(t) = \frac{t_{abs,m} \times D_m}{k_{pré\_all}} \times \left(1 - e^{-k_{pré\_all} \times t_{pré\_all}}\right) \times e^{-(k_{pré\_all} + k_{all}) \times (t - t_{pré\_all})}$$
$$+ \frac{t_{abs,m} \times D_m}{k_{pré\_all} + k_{all}} \times \left(1 - e^{-(k_{pré\_all} + k_{all}) \times (t - t_{pré\_all})}\right)$$

Equation 2.4.9

The concentration in breast milk at time t (> $t_{pré\_all}$) can be calculated using the following differential equation:

$$\frac{dm_{lait\_mat}}{dt} = k_{all} \times m_m$$

Equation 2.4.10

where m_{lait_mat}: mass of pollutant eliminated in breast milk,

or $\quad C_{lait\_mat} \times \dfrac{dM_{lait\_mat}}{dt} + M_{lait\_mat} \times \dfrac{dC_{lait\_mat}}{dt} = k_{all} \times m_m$

Equation 2.4.11

where M_{lait_mat}: mass of milk produced by the mother from instant $t_{pré\_all}$.

If over the period ΔT considered, concentration variations in the milk are negligible, we can state:

and $\quad C_{lait\_mat}(\Delta T) = \dfrac{k_{all} \times m_m \times \Delta T}{M_{lait\_mat}(t) - M_{lait\_mat}(t - \Delta T)}$

Equation 2.4.12

If ΔT equals one day and if the quantity of milk produced per day by the mother equals I_{nour_lait}, the average concentration at day j in the breast milk is given by:

$$C_{lait\_mat,moy\_j} = \frac{k_{all} \times m_m(t)}{I_{nour\_lait}}$$

Equation 2.4.13

If $t_{abs,m}$, D_m, $k_{pré\_all}$ and k_{all} are constant, we can state:

$$C_{lait\_mat,moy\_j} = \frac{k_{all} \times t_{abs,m} \times D_m}{I_{nour\_lait} \times k_{pr\acute{e}\_all}} \times \left(1 - e^{-k_{pr\acute{e}\_all} \times t_{pr\acute{e}\_all}}\right) \times e^{-(k_{pr\acute{e}\_all} + k_{all}) \times (t - t_{pr\acute{e}\_all})}$$

$$+ \frac{k_{all} \times t_{abs,m} \times D_m}{I_{nour\_lait} \times (k_{pr\acute{e}\_all} + k_{all})} \times \left(1 - e^{-(k_{pr\acute{e}\_all} + k_{all}) \times (t - t_{pr\acute{e}\_all})}\right)$$

Equation 2.4.14

The average pollutant concentration in breast milk during the breast-feeding period (T$_{all}$) is obtained by integrating equation 2.4.10 over the entire breast-feeding period:

$$\overline{C_{lait\_mat}} = \frac{k_{all} \times t_{abs,m} \times D_m}{I_{nour\_lait} \times (k_{pr\acute{e}\_all} + k_{all})} \times \left[\frac{1}{T_{all}} \times \left(\frac{1 - e^{-k_{pr\acute{e}\_all} \times t_{pr\acute{e}\_all}}}{k_{pr\acute{e}\_all}} - \frac{1}{k_{pr\acute{e}\_all} + k_{all}} \right) \times \left(1 - e^{-(k_{pr\acute{e}\_all} + k_{all}) \times T_{all}}\right) + 1 \right]$$

Equation 2.4.15

Symbol	Parameters	Dimensions	Units	Status
$C_{lait\_mat\_moy\_j}$	Average pollutant concentration in the breast milk at day j	M.M^{-1}	mg.kg^{-1}	C or E
m$_m$ (t)	Mass of pollutant in the mother's body at day j	M	mg	C
$\overline{C_{lait\_mat}}$	Average pollutant concentration in the breast milk during the breast-feeding period (T$_{all}$)	M.M^{-1}	mg.kg^{-1}	C or E
I$_{nour\_lait}$	Quantity of breast milk ingested by the baby	M.T^{-1}	kg.d^{-1}	C or E
$\overline{I_{nour\_lait}}$	Average quantity of breast milk ingested by the baby during the breast-feeding period (T$_{all}$)	M.T^{-1}	kg.d^{-1}	C or E
D$_m$	Quantity of pollutant to which the mother is exposed per day (daily external exposure dose multiplied by the mother's body mass)	M.T^{-1}	mg.d^{-1}	C or E
t$_{abs,m}$	Absorption rate of the pollutant by the mother	-	-	E
k$_{pr\acute{e}\_all}$	Pollutant loss coefficient from the mother's body excluding breast-feeding	T^{-1}	d^{-1}	E
k$_{all}$	Pollutant elimination coefficient to the breast milk	T^{-1}	d^{-1}	E
T$_{all}$	Breast-feeding period	T	d	E

Comments:

1. The approach requires prior data on the elimination coefficient for the pollutant studied into breast milk.

2. The average pollutant concentration in breast milk at day j (C$_{lait\_mat,moy\_j}$) can be calculated using the same approach as above, with parameters (D$_m$, k$_{all}$) varying with time, by integrating $\frac{dm_{lait\_mat}}{dt}$ over time increments where these parameters can be considered as constant.

2.4.1.2.2. ESTIMATE USING THE US EPA APPROACH

This approach, used by Smith et al. (1987) and Sullivan et al. (1991) for dioxins and furans, substances present almost exclusively in fats, is based on the

assumption of equality between the pollutant concentrations in the lipid phase of breast milk and the mother's fat tissues. The pollutant transfer rate to the breast milk is defined here as a function of the quantity of milk excreted.

By making a few modifications, US EPA (1998) extended this approach to other substances.

The concentration in breast milk (C_{lait_mat}) is then calculated as follows:

$$C_{lait\_mat} = f_{lip\_lait\_mat} \times C_{lip\_lait\_mat} + (1 - f_{lip\_lait\_mat}) \times C_{aq\_lait\_mat}$$

Equation 2.4.16

Symbol	Parameters	Dimensions	Units	Status
C_{lait_mat}	Pollutant concentration in the breast milk	M.M^{-1}	mg.kg^{-1}	C or E
$C_{aq\_lait\_mat}$	Pollutant concentration in the aqueous phase of breast milk	M.M^{-1}	mg.kg^{-1}	C or E
$C_{lip\_lait\_mat}$	Pollutant concentration in the lipid phase of breast milk	M.M^{-1}	mg.kg^{-1}	C or E
$f_{lip\_lait\_mat}$	Mass fraction of lipids in breast milk	-	-	E

For very lipophilic substances, the pollutant concentration in the aqueous fraction of the milk is negligible and conversely, for salts and metals, the pollutant concentration in the lipid phase of the milk can be ignored.

2.4.1.2.2.1. CONCENTRATION IN THE LIPID FRACTION OF BREAST MILK

It can be stated:

$$C_{m\_lip} = \frac{f_{lip} \times C_m}{f_{m\_lip}}$$

Equation 2.4.17

where C_{m_lip}: pollutant concentration in the lipid phase of the mother's body,

C_m: pollutant concentration in the mother's body,

f_{m_lip}: mass fraction of lipids in the mother's body,

f_{lip}: mass fraction of pollutant in lipids in the mother's body.

f_{lip} is generally defined empirically from absorption and distribution studies. For lipophilic substances, f_{m_lip} can be greater than 90%.

From equation 2.4.9 (which assumes that $t_{abs,m}$, D_m, $k_{pré\_all}$ and k_{all} are **constant over the mother's exposure period)**, the pollutant concentration in the mother's body (C_m) after the start of breast-feeding is given by:

$$C_m(t) = \frac{t_{abs,m} \times D_m}{k_{pre\_all} \times B_{w,m}} \left(1 - e^{-k_{pré\_all} \times t_{pré\_all}}\right) \times e^{-(k_{pré\_all} + k_{all}) \times (t - t_{pré\_all})}$$

$$+ \frac{t_{abs,m} \times D_m}{(k_{pré\_all} + k_{all}) \times B_{w,m}} \left(1 - e^{-(k_{pré\_all} + k_{all}) \times (t - t_{pré\_all})}\right)$$

Equation 2.4.18

where D_m: quantity of pollutant to which the mother is exposed per day,

k_{all}: pollutant elimination coefficient to breast milk,

$k_{pré\_all}$: pollutant loss coefficient, excluding breast-feeding,

$t_{abs,m}$: pollutant absorption rate by the mother,

$t_{pré\_all}$: breast-feeding start date,

$B_{w,m}$: body mass of the mother.

As the concentration in the lipids of the mother's milk ($C_{lip\_lait\_mat}$) is assumed equal to the concentration in the lipids of the mother's body (C_{m_lip}), the above equation is used to estimate $C_{lip\_lait\_mat}$. Hence:

$$C_{lip\_lait\_mat}(t) = \frac{f_{lip}}{f_{m\_lip}} \times \frac{t_{abs,m} \times D_m}{B_{w,m}} \times \left[\frac{1-e^{-k_{pré\_all} \times t_{pré\_all}}}{k_{pre\_all}} \times e^{-(k_{pré\_all}+k_{all}) \times (t-t_{pré\_all})} + \frac{1-e^{-(k_{pré\_all}+k_{all}) \times (t-t_{pré\_all})}}{k_{pré\_all}+k_{all}} \right] \quad \text{Equation 2.4.19}$$

Comment: **if $t_{abs,m}$, D_m, $k_{pré\_all}$ or k_{all} vary**, the concentration in the milk fat may be calculated over time by integrating equation 2.4.2 over time increments where these variables can be considered as constant. In this case, we have additionally to assume a rapid equilibrium between the pollutant concentration in milk fats and the mother's lipids.

To obtain the average concentration in the milk lipids during the breast-feeding period, equation 2.4.19 must be integrated over this period, thus:

$$\overline{C}_{lip\_lait\_mat} = \frac{1}{T_{all}} \times \int_{t_{pré\_all}}^{T_{all}+t_{pré\_all}} C_{lip\_lait\_mat}(t)dt \quad \text{Equation 2.4.20}$$

where T_{all}: duration of the breast-feeding period

The US EPA (1998) gives the following expression:

$$\overline{C}_{lip\_lait\_mat} = \frac{t_{abs,m} \times D_m \times f_{lip}}{k_{pre\_all} \times B_{w,m} \times f_{m\_lip}} \times \left[\frac{1-e^{-(k_{pré\_all}+k_{all}) \times T_{all}}}{T_{all} \times (k_{pré\_all}+k_{all})} \times \left(1 - \frac{k_{pré\_all}}{k_{pré\_all}+k_{all}} - e^{-k_{pré\_all} \times t_{pré\_all}} \right) + \frac{k_{pré\_all}}{k_{pré\_all}+k_{all}} \right]$$

Equation 2.4.21

Symbol	Parameters	Dimensions	Units	Status
$C_{lip\_lait\_mat}(t)$	Pollutant concentration in lipids in breast milk at time t (t > $t_{pré\_all}$)	M.M^{-1}	mg.kg^{-1}	C or E
$\overline{C}_{lip\_lait\_mat}$	Average pollutant concentration in breast milk lipids during the breast-feeding period (T_{all})	M.M^{-1}	mg.kg^{-1}	C or E
f_{lip}	Mass fraction of pollutant in lipids in the mother's body	-	-	E
f_{m_lip}	Mass fraction of lipids in the mother's body	-	-	E
D_m	Quantity of pollutant to which the mother is exposed per day (daily external exposure dose multiplied by the mother's body mass)	M.T^{-1}	mg.d^{-1}	C or E
$B_{w,m}$	Body mass of the mother	M	kg	E
$t_{abs,m}$	Absorption rate of the pollutant by the mother	-	-	E
$k_{pré\_all}$	Pollutant loss coefficient from the mother's body, excluding breast-feeding	T^{-1}	d^{-1}	E
k_{all}	Pollutant elimination coefficient to the breast milk	T^{-1}	d^{-1}	E
T_{all}	Breast-feeding period	T	d	E
$t_{pré\_all}$	Exposure duration considered before breast-feeding	T	d	E

Expression 2.4.21 is actually an approximation of equation 2.4.20. In fact, this equation assumes that the mother's body mass ($B_{w,m}$), the pollutant fraction stored in the mother's lipids (f_{lip}) and the mass fraction of lipids in the mother's body (f_{m_lip}) are constant (in addition to the parameters $t_{abs,m}$, D_m, $k_{pré\_all}$ and k_{all}) during the mother's exposure period. But these three parameters are likely to change during this period. If the foodstuffs ingested by the mother constitute the main vector for her exposure and if her exposure dose remains constant, f_{m_lip} must, in all likelihood, reduce during the breast-feeding period, leading to an increase in the pollutant concentration in the lipid phase of the mother's body.

A simplified approach also presented by the US EPA (and taken up by Smith, 1987) consists of estimating C_m and C_{m_lip} **under steady state conditions**, without considering pollutant losses associated with breast-feeding.

From equation 2.4.2, we can therefore state:

$$m_m = \frac{t_{abs,m} \times D_m}{k_{pré\_all}}$$

Equation 2.4.22

and $\quad C_{lip\_lait\_mat} = \frac{t_{abs,m} \times D_m}{k_{pré\_all} \times B_{w,m}} \times \frac{f_{lip}}{f_{m\_lip}}$

Equation 2.4.23

Symbol	Parameters	Dimensions	Units	Status
$C_{lip\_lait\_mat}$	Pollutant concentration in the lipids of breast milk	M.M⁻¹	mg.kg⁻¹	C or E
f_{lip}	Mass fraction of pollutant in lipids in the mother's body	-	-	E
f_{m_lip}	Mass fraction of lipids in the mother's body	-	-	E
D_m	Quantity of pollutant to which the mother is exposed per day (daily external exposure dose multiplied by the mother's body mass)	M.T⁻¹	mg.d⁻¹	C or E
$B_{w,m}$	Body mass of the mother	M	kg	E
$t_{abs,m}$	Absorption rate of the pollutant by the mother	-	-	E
$k_{pré\_all}$	Pollutant loss coefficient from the mother's body, excluding breast-feeding	T⁻¹	d⁻¹	E

Comment: the fact of not considering the elimination constant by milk excretion (k_{all}) and especially by considering steady state conditions as being reached tends to overestimate concentrations in breast milk. This overestimate is all the greater when the pollutant half-life in the body is long and the exposure period before breast-feeding is short. The US EPA showed that if the mother's exposure begins at the same time as breast-feeding and breast-feeding lasts 6 months, expression 2.4.23 gives a concentration for dioxins in the lipid fraction of the milk 18 times greater than that obtained using expression 2.4.21. On the other hand, the overestimation obtained with expression 2.4.23 is no more than a factor 3 compared to relationship 2.4.21, when the mother's exposure duration is 5 years.

2.4.1.2.2.2. Estimating the elimination coefficient

k_{all} can be defined from the following equations:

$$\frac{dm_m}{dt} = t_{abs,m} \times D_m - k_{pré\_all} \times m_m - k_{all} \times m_m \qquad \text{Equation 2.4.24}$$

where m_m: mass of pollutant in the mother's body,

and
$$\frac{dm_m}{dt} = t_{abs,m} \times D_m - k_{pré\_all} \times m_m - I_{nour\_lait} \times C_{lait\_mat} \qquad \text{Equation 2.4.25}$$

where I_{nour_lait}: quantity of milk ingested by the baby per day,

hence
$$k_{all} = \frac{I_{nour\_lait} \times C_{lait\_mat}}{m_m} \qquad \text{Equation 2.4.26}$$

By assumption,

$$\frac{C_{lait\_mat}}{C_m} = \frac{f_{lip} \times f_{lip\_lait\_mat}}{f_{m\_lip}} \qquad \text{Equation 2.4.27}$$

where $f_{lip\_lait\_mat}$: mass fraction of lipids in the breast milk,

hence
$$k_{all} = \frac{I_{nour\_lait}}{B_{w,m}} \times \frac{f_{lip} \times f_{lip\_lait\_mat}}{f_{m\_lip}} \qquad \text{Equation 2.4.28}$$

Symbol	Parameters	Dimensions	Units	Status
k_{all}	Pollutant elimination coefficient to the breast milk	T^{-1}	d^{-1}	E
$B_{w,m}$	Body mass of the mother	M	kg	E
f_{lip}	Mass fraction of pollutant in lipids in the mother's body	-	-	E
f_{m_lip}	Mass fraction of lipids in the mother's body	-	-	E
$f_{lip\_lait\_mat}$	Mass fraction of lipids in breast milk	-	-	E
I_{nour_lait}	Quantity of milk ingested by the baby per day	$M.T^{-1}$	$kg.d^{-1}$	E

2.4.1.2.2.3. CONCENTRATION IN THE AQUEOUS FRACTION OF THE MILK

The approach developed by the US EPA (1998) assumes that the concentration in the aqueous phase of breast milk is proportional to the concentration in the mother's plasma. Pollutants present in the red blood cells are considered as unavailable for transfer to the breast milk. The concentration in the aqueous phase of the milk is therefore given by:

$$C_{aq\_lait\_mat} = P_{lm\_pl} \times C_{m\_pl}$$

Equation 2.4.29

where $C_{aq\_lait\_mat}$: concentration in the aqueous fraction of the milk,

P_{lm_pl}: partition coefficient of the pollutant between the mother's plasma and aqueous phase of the milk,

C_{m_pl}: pollutant concentration in the mother's plasma,

and $$C_{m\_pl} = f_{pl} \times \frac{C_m}{f_{m\_pl}}$$

Equation 2.4.30

where C_m: pollutant concentration in the mother's body,

f_{pl}: mass fraction of pollutant in the plasma,

f_{m_pl}: mass fraction of plasma in the mother's body.

Like f_{lip}, f_{pl} can vary with time. Given the difficulty of defining f_{pl} over time, the US EPA estimated the concentration in the aqueous phase of the milk ($C_{aq\_lait\_mat}$) **under steady state conditions**, from the pollutant concentration in the mother's body (C_m) under steady state conditions and without taking account of losses associated with breast feeding, hence:

$$C_{aq\_lait\_mat} = \frac{t_{abs,m} \times D_m \times P_{lm\_pl}}{k_{pré\_all} \times B_{w,m}} \times \frac{f_{pl}}{f_{m\_pl}}$$

Equation 2.4.31

Symbol	Parameters	Dimensions	Units	Status
$C_{aq\_lait\_mat}$	Pollutant concentration in the aqueous phase of the milk	$M.M^{-1}$	$mg.kg^{-1}$	C or E
D_m	Quantity of pollutant to which the mother is exposed per day (daily external exposure dose multiplied by the mother's body mass)	$M.T^{-1}$	$mg.d^{-1}$	C or E
$t_{abs,m}$	Absorption rate of the pollutant by the mother	-	-	E
P_{lm_pl}	Partition coefficient of the pollutant between the mother's plasma and aqueous phase of the milk	-	-	E
$k_{pré\_all}$	Pollutant loss rate from the mother's body, excluding breast-feeding	T^{-1}	d^{-1}	E

Ref: DRC-14-141968-04378A

$B_{w,m}$	Body mass of the mother	M	kg	E
f_{pl}	Mass fraction of pollutant in the plasma	-	-	E
f_{m_pl}	Mass fraction of plasma in the mother's body	-	-	E

The mass fraction of pollutant in the plasma (f_{pl}) under steady state conditions may be estimated from the mass fraction of the pollutant in the blood (data can be obtained from studies of pollutant absorption and distribution in the body).

Thus, we can state:

$$f_{pl} = f_{sang} - f_{gl}$$

Equation 2.4.32

where f_{sang}: mass fraction of pollutant present in the blood,

f_{gl}: mass fraction of pollutant present in the red blood cells.

If P_{gl_pl} is the pollutant partition coefficient between red blood cells and the plasma (ratio of mass concentrations of pollutant between red blood cells and the plasma),

then $$f_{pl} = f_{sang} - \frac{P_{gl\_pl} \times f_{pl} \times (1 - f_{sang\_pl})}{f_{sang\_pl}}$$

Equation 2.4.33

and $$f_{pl} = \frac{f_{sang} \times f_{sang\_pl}}{f_{sang\_pl} + P_{gl\_pl} \times (1 - f_{sang\_pl})}$$

Equation 2.4.34

where f_{sang_pl}: plasma fraction in the blood.

Comment: values must be assigned to P_{lm_pl} and P_{gl_pl}, specific to the pollutant studied. According to the US EPA, a default value of 1 can be used for these two parameters for most pollutants.

2.4.1.3. COMMENTS ON CALCULATING THE CONCENTRATION IN BREAST MILK

The models developed above can contain significant uncertainty. Among the sources of uncertainties, we should reference:

- that associated with the assumption of proportionality of the concentration in milk relative to the mother's exposure dose. While at low doses (as might be encountered under environmental conditions), TCDD and other dioxin congeners have demonstrated linear pharmacokinetic behaviour in laboratory animals, at higher doses (toxic doses), these compounds have shown dose-dependent behaviour (Roth et al., 1984, cited by US EPA, 1998). The error associated with using linear mathematical models is not known. The US EPA recommend not using this type of model (and instead using pharmacokinetic models) for pollutants such as lead, which accumulates in bones and for which the distribution in the body is too complex to be represented by this type of approach;

- assuming constant parameters to determine a large number of the equations above. Thus, the quantity of pollutant to which the mother is exposed (D_m) varies with differences in diet and activity generally observed between periods before and after pregnancy and during the breast-feeding period;

- assuming equality between the pollutant concentration in the lipid phase of breast milk and the concentration in the mother's fat tissues, in the approach given by the US EPA. The US EPA states that the fats in breast milk, synthesized by the mammary glands, can have lower pollutant concentrations that the fats stored in the mother's body. However, it considers this assumption reasonable for very lipophilic substances, based on the results of Beck et al. (1994), which showed similar pollutant concentrations of polychlorodibenzodioxins and polychlorodibenzofurans in breast milk fats and fatty tissues;

- assuming that the equilibrium between the pollutant concentration in the mother's lipids and breast milk lipids is established rapidly, while some of the parameters affecting the pollutant concentration in the mother's body are considered as variable over time;

- the uncertainty associated with the values assigned to the parameters of these equations, which can be significant.

So far as we know, the performance of the equations described above has rarely been tested. For lack of accurate data relating to specific contamination sources, background dioxin concentrations measured in breast milk have been compared to those predicted by these models. In 1999, InVS (2000) measured the concentrations of 17 congeners in the breast milk of primiparous women aged 20 to 35 years. Samples taken between 4 and 8 weeks' breast-feeding showed concentrations between 6.5 and 34.5 pg TEQ (toxic equivalent)/g of fat. For a background exposure of 1.31 pg TEQ/kg/d, as estimated by AFSSA in 2000, equation 2.4.20 gives consistent concentrations, between 14 and 21 pg/g. The simplified equation, not considering losses due to breast-feeding (expression 2.4.6 divided by the mass of lipids in the mother), gives essentially-identical results. Conversely, the estimate obtained using a biotransfer coefficient (estimated using a regression relationship (derived by Travis et al, 1988, reported by the US EPA) and the octanol-water partition coefficient) gives a 15-times greater concentration in the milk. The US EPA (1998), using American data, made the same type of comparison and obtained broadly similar results. The US EPA only recommends using the biotransfer coefficient model in the absence of the parameters required to use kinetic models and for long-term exposure of the mother (the overestimate due to assuming steady state conditions is too great for short-term exposure).

2.4.2. EXPOSURE DOSE OF BABIES BY INGESTION OF BREAST MILK

The exposure dose of babies by ingesting breast milk is given by:

$$E_{lait\_mat} = \frac{I_{nour\_lait} \times C_{lait\_mat}}{B_{w,nour}}$$

Equation 2.4.35

The average exposure dose of babies over the exposure period d_{exp_nour} is given by:

$$\overline{E_{lait\_mat}}(d_{\exp\_nour}) = \frac{\sum_{i=1}^{n} E_{lait\_mat}(t_i) \times \Delta t_i}{d_{\exp\_nour}}$$

Equation 2.4.36

where Δt_i: period during which the exposure dose equals $E_{lait\_mat}(t_i)$,

$$\sum_{i=1}^{n} \Delta t_i = T_2 - T_1$$

n: number of time increments,
i: iteration number between 1 and n.

Symbol	Parameters	Dimensions	Units	Status
$\overline{E_{lait\_mat}}(d_{exp\_nour})$	Average exposure dose ingested by the baby via breast milk over the exposure period d_{exp_nour}	$M.M^{-1}.T^{-1}$	$mg.kg^{-1}.d^{-1}$	C
$E_{lait\_mat}(t_i)$	Exposure dose ingested by the baby via breast milk at time t_i	$M.M^{-1}.T^{-1}$	$mg.kg^{-1}.d^{-1}$	C
Δt_i	Period during which the exposure dose equals $E_{lait\_mat}(t_i)$	T	d	E
d_{exp_nour}	Duration of the baby's exposure period	T	d	C or E
T_1	Beginning of the exposure period	T	d	E
T_2	End of the exposure period	T	d	E
$B_{w,nour}$	Body mass of the baby	M	kg	E
I_{nour_lait}	Quantity of breast milk ingested by the baby	$M.T^{-1}$	$kg.d^{-1}$	E
C_{lait_mat}	Pollutant concentration in the breast milk	$M.M^{-1}$	$mg.kg^{-1}$	C or E

2.5. EXPOSURE BY DERMAL CONTACT

Dermal exposure can produce systemic effects after absorption or local effects in the skin (allergic reactions, skin cancer, etc.). The issue of local effects assumes calculation of an external exposure dose (or *intake*). This point is covered in section 2.5.4.1. In contrast, taking account of systemic effects assumes calculating the internal dose (or *uptake*) and is the main subject of the developments below.

2.5.1. MODELLING DERMAL ABSORPTION: GENERAL REMARKS AND PRINCIPLES

Dermal exposure can occur by contact with the pollutant:

- in the pure phase,
- dissolved in water,
- adsorbed to soil particles,
- in gaseous form.

Dermal absorption of an environmental contaminant from gaseous pollutant is not considered, because only pollutants with a sufficiently high vapour pressure can penetrate the skin, and in this case respiratory exposure is still preponderant (this may be different in the working environment, when people exposed are wearing a respiratory mask).

The exposure of individuals to a pure phase pollutant is not the chronic exposure situation traditionally studied in risk assessments associated with contamination of a site or emissions from a registered facility for environmental protection. It may be acute exposure, for example during decontamination work. In this case the uptake can be estimated for a specific absorption rate, as for exposure during contact with polluted soil (cf. section 2.5.3.1), but with an absorption rate correlating to the pure phase.

The approaches developed below therefore correspond to exposure by contact with contaminated water (bath, swimming, etc.) or contaminated soil (soil particles deposited on exposed parts of the body).

Pollutants can be absorbed by transepidermal (trans-cellular and inter-cellular) and pilosebaceous pathways. The second is often considered as negligible compared to the first (Scheuplein and Blank 1971, cited in US EPA 1992).

The skin comprises two layers:

- the epidermis, non-vascular layer about 100 µm thick,
- the dermis, highly vascular layer 500 to 3000 µm thick, when the pores and hairs originate.

The external surface of the epidermis is made up of dead, keratinised and partially-dried cells. This layer, 10 to 40 µm thick, is called the keratinous layer (or *stratum corneum*). It is made up from proteins, lipids and water, and is assumed to represent the principal barrier to dermal absorption of pollutants.

A substance applied on the skin penetrates the stratum corneum by diffusion, but part of the quantity applied can evaporate, bind irreversibly to the stratum corneum or be metabolised.

In addition to the elements defining the intensity of contact with the skin (characteristics of the source matrix, pollutant concentration in the matrix, quantity of soil on the skin, contact time), factors influencing dermal absorption are associated with:

- the physico-chemical properties of the substance, particularly:
    - lipophilic nature: lipophilic substances penetrate the skin better than hydrophilic substances (maximum penetration for substances where log K_{ow} is between +1 and +2),
    - ionic structure: highly ionised compounds diffuse very poorly through the stratum corneum,
    - polarity: non-polar substances penetrate more easily than polar substances,
    - molecular weight: low molecular weight substances penetrate the skin better,
    - volatility, due to competition between absorption and evaporation of the substance at the surface of the skin;
- characteristics of the skin, such as:
    - skin temperature,
    - the level of skin hydration (increases dermal absorption),
    - area of the body (areas with varying degrees of hydration or permeability, etc.),
    - condition and age of the skin.

The general approach consists of estimating the dose of absorbed pollutant, either from an absorption speed (also called the permeability coefficient) or from an absorption rate.

2.5.2. POLLUTANT ABSORPTION FROM CONTAMINATED WATER

If the skin is not damaged, if its characteristics are not modified over time and if the pollutant is not actively transported, Fick's First Law can be used to represent the steady-state flux of pollutant passing through the skin.

If the pollutant concentration in the water is constant and if the pollutant concentration in the body is negligible during contact with the water, pollutant flux through the skin per unit time and unit area (J_{cut}) is:

$$J_{cut} = K_p \times C_{eau}$$

Equation 2.5.1

where C_{eau}: pollutant concentration in the water,

K_p: dermal permeability coefficient of the pollutant in the water.

The dermal permeability coefficient then equals to the inverse of the sum of resistances of the stratum corneum and viable epidermis against passage of the pollutant, or:

$$\frac{1}{K_p} = \frac{1}{K_{p,cc}} + \frac{1}{K_{p,ev}}$$

Equation 2.5.2

where $K_{p,cc}$: permeability coefficient of the pollutant in the water through the stratum corneum,

and $K_{p,ev}$: permeability coefficient of the pollutant in the water through the viable epidermis.

If there is an instantaneous equilibrium between the water and external surface of the stratum corneum, or if the thickness of the boundary layer between the water environment and the skin tends to 0 (turbulent conditions), then

$$K_{p,cc} = \frac{K_{cc\_eau} \times D_{cc}}{L_{cc}}$$

Equation 2.5.3

where K_{cc_eau}: partition coefficient of the pollutant between the stratum corneum and water,

D_{cc}: diffusion coefficient of the pollutant in the stratum corneum,

L_{cc}: thickness of the stratum corneum.

Similarly,

$$K_{p,ev} = \frac{K_{ev\_eau} \times D_{ev}}{L_{ev}}$$

Equation 2.5.4

where K_{ev_eau}: partition coefficient of the pollutant between the viable epidermis and water,

D_{ev}: diffusion coefficient of the pollutant in the viable epidermis,

L_{ev}: thickness of the viable epidermis.

But this approach, applicable to the steady state, may underestimate the quantity of pollutant absorbed following contact with contaminated water, because the steady state is not reached immediately. For a certain time, the quantity of pollutant entering the stratum corneum is actually greater than leaving it. For very lipophilic substances, the layer of the viable epidermis represents a significant resistance and this period can last several hours. Absorption of the pollutant by the viable epidermis can continue after contact with the contaminated water has finished. Estimating the exposure uptake must therefore be based on the total quantity of pollutant absorbed, including the quantity that has entered but not yet left the stratum corneum at the end of the period of contact with the water.

A two-compartment model can be used to represent pollutant absorption through the skin from contaminated water. But solving this model is complex. Cleek and Bunge (1993, 1995) therefore proposed two algebraic expressions to approximate this solution, the choice between one or the other depending on the contact time with the contaminated water. These equations, presented below, were reproduced by US EPA (1992, 2004d) for organic substances.

2.5.2.1. ORGANIC SUBSTANCES

For short contact times with the contaminated water, the pollutant only penetrates a small distance into the stratum corneum. In this situation, the resistance associated with the barrier between the stratum corneum and the living part of the epidermis does not have an influence and the pollutant flux is markedly greater than it would be at steady state.

The incoming pollutant flux can therefore be modelled as if there were a semi-infinite stratum corneum. The quantity of pollutant absorbed per unit of exposed area (DA_{eau}) is therefore:

$$DA_{eau} = 2 \times K_{cc\_eau} \times C_{eau} \times \sqrt{\frac{D_{cc} \times T_{cc}}{\pi}}$$

Equation 2.5.5

where T_{cc}: contact time with contaminated water.

For longer contact times with contaminated water and when steady state is reached, the solution to the two-compartment model representing the stratum corneum and viable epidermis is simplified. Cleek and Bunge (1993) give the following expression:

$$DA_{eau} = \frac{C_{eau} \times L_{cc} \times K_{cc\_eau}}{1+B} \times \left(\frac{D_{cc} \times T_{cc}}{L_{cc}^2} + \frac{(1+3 \times B + 3 \times B^2)}{3 \times (1+B)} \right)$$

Equation 2.5.6

where $B = \dfrac{K_{p,cc}}{K_{p,ev}}$

Equation 2.5.7

Cleek and Bunge therefore propose using expression 2.5.5 to estimate the exposure dose linked to contact with water for a shorter period than the time needed to reach steady flux and expression 2.5.6 when the contact time is longer. The transition point (t*) between using one or other of these expressions is determined by minimising the difference between the exact mathematical solution to the two-compartment model and the two simplified expressions proposed by Cleek and Bunge.

When B > 0.6, equations 2.5.5 and 2.5.6 give the same quantity of absorbed pollutant for:

$$t^* = \left(b - \sqrt{b^2 - c^2} \right) \times \frac{L_{cc}^2}{D_{cc}}$$

Equation 2.5.8

where $b = \dfrac{2 \times (1+B^2)}{\pi} - c$

Equation 2.5.9

and $c = \dfrac{1+3 \times B + 3 \times B^2}{3 \times (1+B)}$

Equation 2.5.10

When B ≤ 0.6, minimum error is obtained with:

$$t^* = \frac{0,4 \times L_{cc}^2}{D_{cc}}$$

Equation 2.5.11

Bunge and Cleek (1995) provide several estimates for B. Their recommended choice is obtained by:

$$B = \frac{K_{p,cc}}{K_{p,ev}} = K_{p,cc} \times \frac{L_{ev}}{D_{ev} \times K_{ev\_eau}}$$

Equation 2.5.12

where $L_{ev} = 10^{-4}$ m

and $K_{ev\_eau} = 1$ (because the epidermis is assumed to behave essentially like water).

For comparably-sized solvent and solute molecules, Bunge and Cleek (1995) report that the diffusion coefficient is inversely proportional to the molar mass of the solute and Tinsley et al. (1979) and Schwarzenbach et al. (1993) give the following relationship: $D_{ev,i} = D_{ev,j} \times \sqrt{\dfrac{M_j}{M_i}}$

where D_i, D_j, M_i and M_j are the diffusion coefficients for substances i and j, and the molar masses for substance i and j, respectively.

Bunge and Cleek (1995) then assumed a diffusion coefficient in the viable epidermis (D_{ev}) of 10^{-10} m^2.s^{-1} (a value 10 times less than for water) for a substance with a molar mass (M) of 50 g.mol$^-$

[1] (consistent with the mean value of 10^{-11} m^2.s^{-1} reported by Tojo et al. for molar masses between 170 and 490 g.mol^{-1}), hence:

$$D_{ev} = 7,1.10^{-10} / \sqrt{M}$$

Equation 2.5.13

and $$B = K_{p,cc} \times \frac{\sqrt{M}}{7,1.10^{-6}}$$

Equation 2.5.14

The US EPA (1992, 2004d) suggests the following variable:

$$\tau_{lag} = \frac{L_{cc}^2}{6 \times D_{cc}}$$

Equation 2.5.15

When B ≤ 0.6, the time taken to reach steady state is therefore estimated by expression 2.5.11 or:

$$t^* = 2,4 \times \tau_{lag}$$

Equation 2.5.16

and when B > 0.6, it is estimated by expression 2.5.8 or:

$$t^* = 6 \times \tau_{lag} \times \left(b - \sqrt{b^2 - c^2} \right)$$

Consequently, when the dermal contact time with contaminated water is less than t*, the dose of absorbed pollutant is estimated by expression 2.5.5 or:

$$DA_{eau} = 2 \times K_{p,cc} \times C_{eau} \times \sqrt{\frac{6 \times \tau_{lag} \times T_{cc}}{\pi}}$$

Equation 2.5.17

When the dermal contact time with contaminated water is greater than t*, the dose of absorbed pollutant is estimated by expression 2.5.6 or:

$$DA_{eau} = K_{p,cc} \times C_{eau} \times \left(\frac{T_{cc}}{1+B} + \frac{2 \times \tau_{lag} \times (1 + 3 \times B + 3 \times B^2)}{(1+B)^2} \right)$$

Equation 2.5.18

Symbol	Parameters	Dimensions	Units	Status
DA$_{eau}$	Mass of pollutant absorbed by dermal contact with contaminated water per unit area	M.L^{-2}	mg.m^{-2}	C or E
K$_{p,cc}$	Dermal permeability coefficient of the pollutant in the water through the stratum corneum	L.T^{-1}	m.s^{-1}	C
C$_{eau}$	Pollutant concentration in water during the dermal contact time	M.L^{-3}	mg.m^{-3}	C or E
T$_{cc}$	Dermal contact time with contaminated water	T	s	E
τ$_{lag}$	'Lag time'	T	s	C
D$_{cc}$	Diffusion coefficient of the pollutant in the stratum corneum	L^2.T^{-1}	m^2.s^{-1}	C
L$_{cc}$	Length of diffusion path in the stratum corneum	L	m	E
B	Ratio of the permeability coefficient for the pollutant through the stratum corneum to the permeability coefficient for the pollutant through the viable epidermis	-	-	C

Comments:

1. In this approach, the uptake is greater than that crossing the skin and reaches the bloodstream during the contact time with contaminated water. Absorption is actually assumed to be able to continue although contact with the contaminated has finished. This approach is more appropriate than a steady state approach for representing the exposure uptake associated with relatively brief dermal contact, as occurs as a result of taking a bath or swimming.

2. However, for substances with very long lag time, the US EPA considers that part of the pollutant contained in the skin may be lost due to skin cells being shed. For this reason, equations 2.5.17 and 2.5.18 in the US EPA 2004 document include an additional factor FA ranging from 0 to 1, representing the pollutant fraction able to be effectively absorbed compared to the quantity present in the skin. The US EPA (2004d) gives value of FA for 209 different pollutants. According to the US EPA, shedding skin cells can have an impact on the quantities of pollutant absorbed when a substance has log K_{ow} greater than 3.5 or when the contact time with contaminated water is more than 10 hours.

3. Without measurements to define the diffusion coefficient in the stratum corneum (D_{cc}), used in equations 2.5.5, 2.5.6, 2.5.8, 2.5.11 and 2.5.15, the value assigned to this parameter is generally estimated from an empirical relationship giving the dermal permeability coefficient ($K_{p,cc}$) based on the octanol-water partition coefficient (K_{ow}) and the molar mass of the pollutant (Potts and Guys relationship or modified Potts and Guys relationship: see US EPA 1992 and 2004, as well as future documents on the physico-chemical parameters of substances). For purposes of consistency, the US EPA also recommends using this relationship to estimate the dermal permeability coefficient for organic substances instead of data from measurements (Vecchia, 1997, also showed that experimental data often varied by 1 or 2 orders of magnitude).

2.5.2.2. INORGANIC SUBSTANCES

The non-steady state approach developed for organic substances does not apply to inorganic substances. The US EPA recommends using the approach based on Fick's First Law, which assumes that a steady state has been reached, or:

$$DA_{eau} = K_{p,cc} \times C_{eau} \times T_{cc} \qquad \text{Equation 2.5.19}$$

In fact, the stratum corneum has low affinity for inorganic substances and stores very little of them. Moreover, the viable epidermis is not a significant barrier to inorganic substances. Steady state is therefore reached rapidly.

Mathematically, it will be noted that if τ_{lag} and B ($= \dfrac{K_{p,cc}}{K_{p,ev}}$) tend to zero, equation 2.5.18 then tends to expression 2.5.19.

Symbol	Parameters	Dimensions	Units	Status
DA_{eau}	Mass of pollutant absorbed by dermal contact with contaminated water per unit area	$M.L^{-2}$	$mg.m^{-2}$	C or E
$K_{p,cc}$	Dermal permeability coefficient of the pollutant in the water through the stratum corneum	$L.T^{-1}$	$m.s^{-1}$	C
C_{eau}	Pollutant concentration in water during the dermal contact time	$M.L^{-3}$	$mg.m^{-3}$	C or E
T_{cc}	Dermal contact time with contaminated water	T	s	E

2.5.2.3. CONDITIONS FOR APPLYING THE MODEL AND ASSOCIATED UNCERTAINTIES

In particular, the equations developed above assume that pollutant transport through the skin is passive, that the membrane properties (stratum corneum and viable epidermis) are not modified by water or the pollutant and that the concentration in water is constant throughout the contact time.

It is not therefore appropriate to use equations 2.5.5, 2.5.6, 2.5.17, 2.5.18 and 2.5.19 with an estimate of the concentration in water (C_{eau}) that varies during the exposure event under consideration. As a result, if the pollutant in the water can evaporate (as may happen when taking a shower) or be adsorbed onto particles or another substrate during the contact period, then with the concentration in water at the beginning of contact these equations will tend to overestimate exposure.

If the pollutant is in dissolved phase and particulate phase in the water, using the pollutant concentration in the water in dissolved and particulate forms, as shown in the above equations, may be a significant overestimate, since dermal absorption of pollutants adsorbed on particles suspended in the water is far less than for pollutants in dissolved form. Nonetheless this approach is recommended by the US EPA (2004d). If the pollutant dose estimated in this way appears to be a sensitive component of exposure, this aspect should be reviewed when evaluating uncertainties.

Furthermore, for partially ionised organic substances, the US EPA (2004d) states that the quantity of pollutant absorbed dermally must be calculated as the sum of the quantities of pollutant absorbed in both non-ionised and ionised forms. Equations 2.5.17 or 2.5.18 (for non-ionised species) and equation 2.5.19 (for ionised species) must therefore be used with the permeability coefficient and pollutant concentration in the water for each species considered.

If φ represents the non-ionised fraction, the concentrations in water to be taken into account in the equations are therefore:

- C_{eau} x φ for the non-ionised fraction,
- C_{eau} x (1 - φ) for the ionised fraction.

The expression for φ is given, for example, in Trapp et al. 1997. It will be reproduced in future documents about the physico-chemical parameters of substances.

Modelling this exposure pathway is recognised as being particularly uncertain. The uncertainties are associated with the modelling assumptions, mathematical form and the values for parameters used in the model.

It is better first to recall that the equations given above for organic substances are simplified solutions of a model representing the diffusion of substances across two membranes of finite thickness. But according to Cleek and Bunge (1993), the maximum difference between the exact solution and the simplified solutions is 13%.

A significant part of the uncertainty associated with the equations developed above to estimate the quantity of pollutant absorbed by contact with contaminated water is very probably linked to the estimate of the permeability coefficient for the substance through the stratum corneum ($K_{p,cc}$).

When measuring $K_{p,cc}$ experimentally, the layer formed by stagnant water on the skin creates resistance to the transfer of pollutant. Under environmental conditions, this resistance is limited by turbulence in the water layer. This difference may therefore lead to underestimating $K_{p,cc}$ for exposure in a bath or shower (cf. McKone et al. 1992 and section 2.5.3.2.2.2 where, for exposure from contaminated soil, the resistance of the boundary layer between the contaminated matrix and the skin is taken into account).

In the relationships presented in section 2.5.2.1, $K_{p,cc}$ is estimated from an empirical relationship established using data measured under *in vitro* conditions (modified Potts and Guys relationship, see US EPA 2004d and future document on the physico-chemical parameters of substances). But certain substances traditionally studied to assess health risks (benzo(a)pyren, tetrachlorodibenzodioxin, etc.) are not included in the valid scope of this relationship. The US EPA also emphasises that the way this relationship has been constructed means it underestimates the permeability coefficients of halogenated substances. According to the US EPA, for substances falling within the scope of validity, the permeability coefficient is estimated with a 95% confidence interval of 1 to 3 orders of magnitude.

Simulations carried out by the US EPA (1998) using the non-steady state model developed above over contact times of 10 minutes, resulted in exposure doses greater than were estimated for ingestion of 2 litres of water per day. This observation suggests the model is over-conservative. However, the assumptions on which these results are based are not clear (particularly the unknown impact of the volatility of the substances studied, which is not included in the model and which may lead to overestimating the dose absorbed by dermal contact). When in doubt, the US EPA recommendation to compare the quantity absorbed from a finite volume of water with that present in this volume of water is certainly appropriate.

However, solely comparing predictions from the model with measured data, carried out by McKone (1993) and reported by the US EPA (2004d) does not reveal the conservative nature of the model. This exercise demonstrated a measured permeability coefficient for chloroform 7 times greater than was modelled and a quantity of pollutant absorbed following dermal contact 5 times greater than modelled.

2.5.3. POLLUTANT ABSORPTION FROM CONTAMINATED SOIL

The knowledge and data available for estimating the pollutant dose absorbed following dermal contact with contaminated soil are still more limited than for contaminated water.

There are two approaches for estimating this transfer:

- one based on using an absorption rate,
- the other based on absorbed flux, calculated from the mass transfer coefficient for the pollutant.

The first approach is recommended by the US EPA (1992, 2004d). Given the little data available to define absorption rates and the uncertainty associated with using them (cf. next section), approaches based on the mass transfer coefficient are also presented in this document. They are not recommended for use as a first approximation, but proposed to provide quantitative information for discussion when assessing uncertainties.

2.5.3.1. ESTIMATE FROM THE ABSORPTION RATE

The exposure dose is calculated from an absorption rate specific to the substance:

$$DA_{sol} = C_{s\_p}(t_{exp\_cut,0}) \times Q_{sol-peau} \times t_{abs\_cut}$$

Equation 2.5.20

Symbol	Parameters	Dimensions	Units	Status
DA_{sol}	Mass of pollutant absorbed by dermal contact with soil per unit area	$M.L^{-2}$	$mg.m^{-2}$	C or E
$C_{s\_p}(t_{exp\_cut,0})$	Pollutant concentration in the soil when deposited on the skin	$M.M^{-1}$	$mg.kg^{-1}$	C or E
Q_{sol_peau}	Soil mass deposited on the skin per unit area (expressed as dry weight, consistent with $C_{s\_p}(t_{exp\_cut,0})$)	$M.L^{-2}$	$kg.m^{-2}$	E
t_{abs_cut}	Dermal absorption rate from the soil	-	-	E

The limitations to this approach are associated with the fact that:

- absorption rates have been defined for few substances. The US EPA 2004 document gives values for 11 substances or substance groups;
- absorption rate depends on exposure conditions (contact time, quantity of soil deposited on the skin per unit area), soil characteristics (organic carbon content, cation exchange capacity, pH, particle size), contamination (pollutant species, age of the contamination, pollutant concentration in the soil, etc.). The experimental conditions from which values for absorption rates have been defined are generally quite different from those encountered under environmental conditions. In particular, soil quantities on the skin per unit area used in experiments are greater than those expected under environmental conditions. As it could be observed that the absorption rate decreased when the quantity of soil on the skin increased beyond the quantity needed to form a continuous thin layer on the skin, the absorption rate under environmental conditions may be greater than the value measured under experimental conditions. Conversely, the values recommended by the

US EPA generally relate to exposure periods of 24 hours and may prove to be overestimated for shorter exposure periods.

Despite the limitations associated with these data, the US EPA recommends in its 2004 document that these absorption rates be used without adjustment to assess the impact of the dermal pathway for contaminated sites.

However, in the initial reference document on assessing dermal risk (1992), the US EPA had proposed methods for adjusting the absorption rate based on the quantity of soil deposited on the skin per unit area and methods for estimating (sometimes overestimating) this absorption rate in the absence of specific measurement data. Given the lack of data and uncertainties associated with existing data, these approaches will be presented in future documents on the physico-chemical parameters of substances, to help identify the uncertainties and for purposes of characterising and discussing them.

2.5.3.2. ESTIMATE BY CALCULATING TRANSFER FLUX

The US EPA (1992) and McKone et al. (1992) developed two similar models for estimating the pollutant dose absorbed by dermal contact with contaminated soil.

The US EPA approach is based on using the permeability coefficient for the substance in water through the stratum corneum, while McKone's approach defines the permeability coefficient from the substance's physico-chemical properties and also takes account of the boundary layer existing between the skin and the soil layer.

Furthermore, since the contact time between the contaminated soil and the skin may be relatively long, these two models take account of pollutant losses over time from the quantity of pollutant initially deposited on the skin. Using the mass balance established for the pollutant deposited on the skin, these models avoid excessive overestimates for the quantities of pollutant absorbed, which could lead to calculating uptakes greater than those deposited.

2.5.3.2.1. US EPA (1992) METHOD

According to this approach, if the concentration in the body is negligible during the period of exposure, the uptake can be calculated using the following expression:

$$J_c = C_{s\_p} \times MV_{s\_p} \times K_p^{sol}$$

Equation 2.5.21

where J_c: absorbed pollutant flux per unit time and area,

C_{s_p}: pollutant concentration in the soil present on the skin,

K_p^{sol} : dermal permeability coefficient of the pollutant in the soil,

MV_{s_p}: density of the soil deposited on the skin.

The US EPA (1992) considers that the pollutant available for dermal absorption is the pollutant in solution in the interstitial water and estimates the dermal permeability coefficient of the pollutant in soil (K_p^{sol}) based on the dermal permeability coefficient of the pollutant in water ($K_{p,cc}$).

In fact, if:

$$J_c = C_{es\_p} \times K_{p,cc}$$

Equation 2.5.22

where C_{es_p}: pollutant concentration in the soil water,

according to equations 2.5.21, 2.5.22 and 1.1.11 **(conditions: pollutant concentration in the soil below the limit of solubility, multi-phase equilibrium reached between the different phases in the soil)**, the following relationship can be stated:

$$K_p^{sol} = \frac{K_{p,cc}}{MV_{s\_p} \times K_d}$$

Equation 2.5.23

where K_d: partition coefficient of the pollutant between the particles soil and water

and $\theta_{s\_p} + \alpha_{s\_p} \times \dfrac{H}{R \times T_{peau}} \prec\prec K_d \times MV_{s\_p}$.

where α_{s_p}: air content of the soil on the skin,

θ_{s_p}: water content of the soil on the skin,

T_{peau}: temperature at the surface of the skin,

H: Henry constant,

R: universal gas constant.

The pollutant concentration in the soil on the skin (C_{s_p}) is determined by taking account of the reduction in pollutant concentration in the soil layer deposited on the skin due to absorption and volatilisation. Thus the pollutant concentration in the soil over time is calculated using the following differential equation:

$$A \times Q_{sol\_peau} \times \frac{dC_{s\_p}}{dt} = -(k_{vol} + k_{abs}) \times C_{s\_p} \times Q_{sol\_peau} \times A$$

Equation 2.5.24

where Q_{sol_peau}: mass of soil deposited on the skin per unit area,

C_{s_p}: pollutant concentration in the soil present on the skin,

A: area of skin exposed,

k_{vol}: mass transfer coefficient by volatilisation,

k_{abs}: mass transfer coefficient by absorption.

hence $C_{s\_p}(t) = C_{s\_p}(t_{exp\_cut,0}) \times e^{-(k_{vol}+k_{abs}) \times t}$ Equation 2.5.25

where $C_{s\_p}(t_{exp\_cut.0})$: pollutant concentration in the soil when deposited on the skin.

Reduction of the pollutant concentration in the soil due to absorption leads to the following equation:

$$k_{abs} \times C_{s\_p} \times Q_{sol\_peau} \times A = MV_{s\_p} \times K_p^{sol} \times C_{s\_p} \times A$$ Equation 2.5.26

hence $k_{abs} = \dfrac{MV_{s\_p} \times K_p^{sol}}{Q_{sol\_peau}}$ Equation 2.5.27

The quantity of pollutant lost by volatilisation leads to the following relationship:

$$k_{vol} \times C_{s\_p} \times Q_{sol\_peau} \times A = \frac{D_a}{d_a} \times C_{as\_p} \times A$$ Equation 2.5.28

where D_a: diffusion coefficient of the pollutant in air,

d_a: thickness of the boundary layer at the air-soil interface,

C_{as_p}: pollutant concentration in the air contained in the soil present on the skin,

and $k_{vol} = \dfrac{D_a}{d_a} \times \dfrac{1}{Q_{sol\_peau}} \times \dfrac{C_{as\_p}}{C_{s\_p}}$ Equation 2.5.29

Yet, according to equation 1.1.12 **(conditions: pollutant concentration in the soil below the limit of solubility, multi-phase equilibrium reached between the different phases in the soil)**:

$$k_{vol} \approx \frac{D_a}{d_a} \times \frac{1}{Q_{sol\_peau}} \times \frac{H}{K_d \times R \times T_{peau}}$$ Equation 2.5.30

where T_{peau}: temperature at the surface of the skin.

The quantity of pollutant absorbed is obtained by integrating equation 2.5.21 over the dermal contact period, i.e.:

$$DA_{sol} = \frac{MV_{s\_p} \times K_p^{sol}}{k_{vol} + k_{abs}} \times C_{s\_p}(t_{exp\_cut,0}) \times \left(1 - e^{-(k_{vol}+k_{abs}) \times T_{cc}}\right)$$ Equation 2.5.31

The absorption rate can be calculated by dividing the uptake by the quantity of pollutant absorbed on the skin, i.e.:

$$t_{abs\_cut} = \frac{MV_{s\_p} \times K_p^{sol}}{Q_{sol\_peau} \times (k_{vol} + k_{abs})} \times \left(1 - e^{-(k_{vol}+k_{abs}) \times T_{cc}}\right)$$ Equation 2.5.32

Symbol	Parameters	Dimensions	Units	Status
DA_{sol}	Mass of pollutant absorbed by dermal contact with soil per unit exposed body area	$M.L^{-2}$	$mg.m^{-2}$	C or E
t_{abs_cut}	Dermal absorption rate	-	-	C or E
$C_{s\_p}(t_{exp\_cut,0})$	Concentration in the soil when deposited on the skin	$M.M^{-1}$	$mg.kg^{-1}$	C or E
Q_{sol_peau}	Soil mass deposited on the skin per unit area (expressed as dry weight, consistent with $C_{s\_p}(t_{exp\_cut,0})$)	$M.L^{-2}$	$kg.m^{-2}$	E
k_{vol}	Mass transfer coefficient by volatilisation	T^{-1}	s^{-1}	C or E
k_{abs}	Mass transfer coefficient by absorption	T^{-1}	s^{-1}	C or E
K_p^{sol}	Dermal permeability coefficient of the pollutant in the soil	$L.T^{-1}$	$m.s^{-1}$	C or E
MV_{s_p}	Density of the soil deposited on the skin	$M.L^{-3}$	$kg.m^{-3}$	E
D_a	Diffusion coefficient of the pollutant in air	$L^2.T^{-1}$	$m^2.s^{-1}$	E
d_a	Thickness of the boundary layer at the air-soil interface	L	m	E
T_{cc}	Duration of contact period with contaminated soil	T	s	E
K_d	Partition coefficient between soil particles and soil water	$L^3.M^{-1}$	$m^3.kg^{-1}$	C or E
H	Henry constant	$L^2.M.T^{-2}.Mol^{-1}$	$Pa.m^3.mol^{-1}$	C or E
R	Universal gas constant	$L^2.M.T^{-2}.K^{-1}.Mol^{-1}$	$8.31\ J.K^{-1}.mol^{-1}$	I
T_{peau}	Temperature at the surface of the skin	K	K	E

Comments:

1. This model does not take account of diffusion of the pollutant in the soil. This amounts to considering diffusion in the air boundary layer and transfer in the stratum corneum, respectively, as limiting phenomena for mass transfer by volatilisation and mass transfer by absorption. This assumption appears acceptable in a majority of cases.

2. The US EPA 1992 document indicates that relationship 2.5.23 assumes that the transfer of pollutant from the soil to the skin primarily involves the pollutant in the interstitial water, while in reality there can also be transfer of pollutant in the gaseous phase and lipid phases present in the soil-skin system.

In fact, this assumption is not necessary because relationship 2.5.23 can also be deduced from the expression for Fick's First Law. If the pollutant concentration in the body can be considered as negligible, Fick's First Law leads to:

$$J_c = \frac{D_{cc}}{L_{cc}} \times C'_{cc}$$
<div align="right">Equation 2.5.33</div>

where D_{cc}: diffusion coefficient of the pollutant in the stratum corneum,

L_{cc}: thicknesses of the stratum corneum,

C'_{cc} : pollutant concentration at the outer surface of the stratum corneum.

If the pollutant concentration in the soil layer is considered to be uniform and the resistance of the boundary layer located between the soil and the skin is negligible, then:

$$\frac{C'_{cc}}{MV_{s\_p} \times C_{s\_p}} = K_{cc\_sol}$$

Equation 2.5.34

where K_{cc_sol}: partition coefficient of the pollutant between the stratum corneum and the soil,

C_{s_p} : pollutant concentration in the soil layer present on the skin.

According to equations 2.5.21, 2.5.33 and 2.5.34, we can state:

$$K_p^{sol} = \frac{D_{cc}}{L_{cc}} \times K_{cc\_sol}$$

Equation 2.5.35

Combining expressions 2.5.3 and 2.5.35 yields:

$$\frac{K_p^{sol}}{K_{p,cc}} = \frac{K_{cc\_sol}}{K_{cc\_eau}} = \frac{C'_{cc}}{MV_{s\_p} \times C_{s\_p}} \times \frac{C_{es\_p}}{C'_{cc}} = \frac{C_{es\_p}}{MV_{s\_p} \times C_{s\_p}}$$

Equation 2.5.36

If the pollutant concentration in the soil is below the limit of solubility, according to the assumed equilibrium of pollutant between the different phases in the soil) and equation 1.1.11:

$$\frac{K_p^{sol}}{K_{p,cc}} \approx \frac{1}{MV_{s\_p} \times K_d}$$

Equation 2.5.37

where $\theta_{s\_p} + \alpha_{s\_p} \times \dfrac{H}{R \times T_s} \prec\prec K_d \times MV_{s\_p}$

2.5.3.2.2. McKone et al. method

In this approach, McKone et al. (1992) define the speed of absorption based on the chemical properties of the pollutant, soil and skin. Equations developed by the authors introduce the concepts of fugacity and fugacity capacity. These concepts have not been used in the rest of the document, so these equations have been reformulated to avoid using these types of variables. Instead, partition constants have been introduced into the equations.

As in the previous section, the pollutant concentration in the soil on the skin is calculated from a differential equation:

$$A \times Q_{sol\_peau} \times \frac{dC_{s\_p}}{dt} = -\left(K_{sp} + K_{sa}\right) \times C_{s\_p} \times A$$

Equation 2.5.38

where Q_{sol_peau}: mass of soil deposited on the skin per unit area,

C_{s_p}: pollutant concentration in the soil present on the skin,

A: area of skin exposed,

K_{sp}: mass transfer coefficient from soil to the skin,

K_{sa}: mass transfer coefficient from the soil to air.

Compared to the model in the previous section, mass transfer factors (expressed in T^{-1}) are here replaced by mass transfer coefficients (expressed in $M.L^{-2}.T^{-1}$).

From equation 2.5.38:

$$\frac{dC_{s\_p}}{dt} = -\frac{K_{sp} + K_{sa}}{Q_{sol\_peau}} \times C_{s\_p} \qquad \text{Equation 2.5.39}$$

and

$$C_{s\_p}(t) = C_{s\_p}(t_{\exp\_cut,0}) \times e^{-\left(\frac{K_{sp}+K_{sa}}{Q_{sol\_peau}}\right) \times t} \qquad \text{Equation 2.5.40}$$

where $C_{s\_p}(t_{\exp\_cut,0})$: pollutant concentration in the soil when deposited on the skin.

The quantity of pollutant adsorbed is given by:

$$DA_{sol} = \int_0^{T_{cc}} K_{sp} \times C_{s\_p}\, dt \qquad \text{Equation 2.5.41}$$

where T_{cc}: duration of contact period,

hence

$$DA_{sol} = \frac{Q_{sol\_peau}}{K_{sp} + K_{sa}} \times K_{sp} \times C_{s\_p}(t_{\exp\_cut,0}) \times \left(1 - e^{-\left(\frac{K_{sp}+K_{sa}}{Q_{sol\_peau}}\right) \times T_{cc}}\right) \qquad \text{Equation 2.5.42}$$

and the dermal absorption rate is given by:

$$t_{abs\_cut} = \frac{DA_{sol}}{C_{s\_p}(t_{\exp\_cut,0}) \times Q_{sol\_peau}} \qquad \text{Equation 2.5.43}$$

hence

$$t_{abs\_cut} = \frac{K_{sp}}{(K_{sa} + K_{sp})} \times \left(1 - e^{-\left(\frac{K_{sp}+K_{sa}}{Q_{sol\_peau}}\right) \times T_{cc}}\right) \qquad \text{Equation 2.5.44}$$

Symbol	Parameters	Dimensions	Units	Status
DA_{sol}	Mass of pollutant absorbed by dermal contact with soil per unit exposed body area	$M.L^{-2}$	$mg.m^{-2}$	C or E
t_{abs_cut}	Dermal absorption rate	-	-	C or E
$C_{s\_p}(t_{exp\_cut,0})$	Pollutant concentration in the soil when deposited on the skin	$M.M^{-1}$	$mg.kg^{-1}$	C or E
Q_{sol_peau}	Dry soil mass deposited on the skin per unit area (expressed as dry weight, consistent with $C_{s\_p}(t_{exp\_cut,0})$)	$M.L^{-2}$	$kg.m^{-2}$	E
K_{sa}	Mass transfer coefficient from the soil to air (cf. section 2.5.3.2.2.1)	$M.L^{-2}.T^{-1}$	$kg.m^{-2}.s^{-1}$	C or E
K_{sp}	Mass transfer coefficient from the soil to skin (cf. section 2.5.3.2.2.2)	$M.L^{-2}.T^{-1}$	$kg.m^{-2}.s^{-1}$	C or E
T_{cc}	Duration of contact period with contaminated soil	T	s	E

2.5.3.2.2.1. ESTIMATING THE MASS TRANSFER COEFFICIENT THROUGH THE SOIL LAYER AND AIR BOUNDARY LAYER

K_{sa} is defined using the principle of conservation of mass and by the equality of diffusion flux through the soil layer (J_s) and diffusion flux through the air boundary layer (J_a), located above the layer of soil deposited on the skin.

$$J_s = \frac{DU_{s\_p}}{d_{s\_p}} \times \left(C_{s\_p} - C'_{s\_p}\right)$$

Equation 2.5.45

and $\quad J_a = \frac{D_a}{d_a} \times \left(C'_a - C_a\right)$

Equation 2.5.46

where C'$_{s\_p}$: pollutant concentration in the soil at the interface between the soil layer and the air boundary layer,

C'$_a$: pollutant concentration in the air at the air-soil interface,

D$_a$: diffusion coefficient of the pollutant in air,

d$_a$: thickness of the boundary layer at the air-soil interface,

DU$_{s\_p}$: multiphase diffusion coefficient in the soil layer (as in the expressions developed by McKone et al., this coefficient is expressed relative to the pollutant concentration in the soil),

d$_{s\_p}$: length of the diffusion zone in the soil layer.

Concentrations C'$_{s\_p}$ and C'$_a$ are at equilibrium, according to equation 1.1.12 **(conditions: pollutant concentration in the soil below the limit of solubility, multi-phase equilibrium reached between the different phases in the soil)**, hence:

$$\frac{C'_a}{C'_{s\_p}} = \frac{1}{\dfrac{K_d \times R \times T_{peau}}{H} + \dfrac{\theta_{s\_p} \times R \times T_{peau}}{H \times MV_{s\_p}} + \dfrac{\alpha_{s\_p}}{MV_{s\_p}}}$$

Equation 2.5.47

where θ$_{s\_p}$: water content of the soil layer deposited on the skin,

α$_{s\_p}$: air content of the soil layer deposited on the skin,

K$_d$: partition coefficient between soil particles and soil water,

Ref: DRC-14-141968-04378A

R: universal gas constant,

H: Henry constant,

MV_{s_p}: density of the soil deposited on the skin,

T_{peau}: temperature at the surface of the skin.

Stating $R_g = \dfrac{K_d \times R \times T_{peau}}{H} + \dfrac{\theta_{s\_p} \times R \times T_{peau}}{H \times MV_{s\_p}} + \dfrac{\alpha_{s\_p}}{MV_{s\_p}}$, Equation 2.5.48

where J_a and J_s are equal, thus:

$$C'_{s\_p} = \frac{\dfrac{D_a}{d_a} \times C_a + \dfrac{DU_{s\_p}}{d_{s\_p}} \times C_{s\_p}}{\dfrac{D_a}{d_a \times R_g} \times \dfrac{DU_{s\_p}}{d_{s\_p}}}$$

Equation 2.5.49

and $\quad J_s = \dfrac{\dfrac{D_a}{d_a} \times \dfrac{DU_{s\_p}}{d_{s\_p}}}{\dfrac{D_a}{d_a \times R_g} + \dfrac{DU_{s\_p}}{d_{s\_p}}} \times \left(\dfrac{C_{s\_p}}{R_g} - C_a \right)$

Equation 2.5.50

If the concentration in the air (C_a) is negligible, it follows:

$$J_s = K_{sa} \times C_{s\_p} = \frac{1}{\dfrac{d_a}{D_a} + \dfrac{d_{s\_p}}{DU_{s\_p} \times R_g}} \times \frac{C_{s\_p}}{R_g}$$

Equation 2.5.51

and $\quad K_{sa} = \dfrac{1}{\dfrac{d_a}{D_a} \times \left(\dfrac{K_d \times R \times T_{peau}}{H} + \dfrac{\theta_{s\_p} \times R \times T_{peau}}{H \times MV_{s\_p}} + \dfrac{\alpha_{s\_p}}{MV_{s\_p}} \right) + \dfrac{d_{s\_p}}{DU_{s\_p}}}$ Equation 2.5.52

Symbol	Parameters	Dimensions	Units	Status
K_{sa}	Mass transfer coefficient from the soil to air	$M.L^{-2}.T^{-1}$	$kg.m^{-2}.s^{-1}$	C or E
DU_{s_p}	Multiphase diffusion coefficient in the soil layer (expressed relative to the pollutant concentration in the soil) (cf. section 2.5.3.2.2.3)	$M.L^{-1}.T^{-1}$	$kg.m^{-1}.s^{-1}$	C or E
d_{s_p}	Length of the diffusion zone in the soil layer (cf. section 2.5.3.2.2.5)	L	m	E
MV_{s_p}	Density of the soil deposited on the skin	$M.L^{-3}$	$kg.m^{-3}$	E
D_a	Diffusion coefficient of the pollutant in air	$L^2.T^{-1}$	$m^2.s^{-1}$	E
d_a	Thickness of the boundary layer at the air-soil interface	L	m	E
K_d	Partition coefficient between soil particles and soil water	$L^3.M^{-1}$	$m^3.kg^{-1}$	C or E
θ_{s_p}	Water content of the soil layer deposited on the skin	-	-	E
α_{s_p}	Air content of the soil layer deposited on the skin	-	-	E
H	Henry constant	$L^2.M.T^{-2}.Mol^{-1}$	$Pa.m^3.mol^{-1}$	C or E
R	Universal gas constant	$L^2.M.T^{-2}.K^{-1}.Mol^{-1}$	$8.31\ J.K^{-1}.mol^{-1}$	I
T_{peau}	Temperature at the surface of the skin	K	K	E

K_{sp} is defined from the diffusion flux through the soil layer (J_s: cf. equation 2.5.45) and the diffusion flux through the stratum corneum (J_c: cf. equation 2.5.33).

Furthermore,

$$\frac{C'_{cc}}{C'_{s\_p}} = MV_{s\_p} \times K_{cc\_sol}$$

Equation 2.5.53

where C'$_{cc}$: pollutant concentration in the stratum corneum at the interface between the soil layer and the skin,

C'$_{s\_p}$: pollutant concentration in the soil at the interface between the soil layer and the skin,

K$_{cc\_sol}$: partition coefficient of the pollutant between the stratum corneum and the soil.

By developing the same reasoning as in section 2.5.3.2.2.1, the equality between fluxes J_s and J_c yields:

$$J_c = K_{sp} \times C_{s\_p} = \frac{MV_{s\_p} \times K_{cc\_sol}}{\dfrac{L_{cc}}{D_{cc}} + \dfrac{d_{s\_p}}{DU_{s\_p}} \times MV_{s\_p} \times K_{cc\_sol}} \times C_{s\_p}$$

Equation 2.5.54

hence $$K_{sp} = \frac{1}{\dfrac{L_{cc}}{D_{cc} \times MV_{s\_p} \times K_{cc\_sol}} + \dfrac{d_{s\_p}}{DU_{s\_p}}}$$

Equation 2.5.55

Symbol	Parameters	Dimensions	Units	Status
K_{sp}	Mass transfer coefficient from the soil to the skin	$M.L^{-2}.T^{-1}$	$kg.m^{-2}.s^{-1}$	C or E
DU_{s_p}	Multiphase diffusion coefficient in the soil layer (expressed relative to the pollutant concentration in the soil)	$M.L^{-1}.T^{-1}$	$kg.m^{-1}.s^{-1}$	C or E
d_{s_p}	Length of the diffusion zone in the soil layer (cf. section 2.5.3.2.2.5)	L	m	E
L_{cc}	Thickness of stratum corneum	L	m	E
D_{cc}	Diffusion coefficient in the stratum corneum (expressed relative to the volume concentration of pollutant in the skin): cf. section 2.5.3.2.2.4	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
K_{cc_sol}	Partition coefficient of the pollutant between the stratum corneum and the soil: cf. section 2.5.3.2.2.4	-	-	C or E
MV_{s_p}	Density of the soil deposited on the skin	$M.L^{-3}$	$kg.m^{-3}$	E

2.5.3.2.2.3. ESTIMATING THE MULTIPHASE DIFFUSION COEFFICIENT IN THE SOIL LAYER

The multiphase diffusion coefficient in the soil layer is expressed relative to the pollutant concentration in the soil (C_{s_p}), such that:

$$DU_{s\_p} = D_{es\_p} \times \frac{C_{es\_p}}{C_{s\_p}} + D_{as\_p} \times \frac{C_{as\_p}}{C_{s\_p}}$$

Equation 2.5.56

where D$_{es\_p}$: diffusion coefficient in the water contained in the soil deposited on the skin,

D$_{as\_p}$: diffusion coefficient in the air contained in the soil deposited on the skin,

C_{es_p}: pollutant concentration in the water contained in the soil deposited on the skin,

C_{as_p}: pollutant concentration in the air contained in the soil deposited on the skin.

D_{es_p} and D_{as_p} are defined based on the diffusion coefficients of the pollutant in the water (D_e) and in the air (D_a) and according to the relationships given by Millington and Quirk (1961):

$$D_{es\_p} = D_e \times \frac{\theta_{s\_p}^{\frac{10}{3}}}{n_{s\_p}^2} \qquad \text{Equation 2.5.57}$$

and

$$D_{as\_p} = D_a \times \frac{\alpha_{s\_p}^{\frac{10}{3}}}{n_{s\_p}^2} \qquad \text{Equation 2.5.58}$$

where θ_{s_p}: water content of the soil layer deposited on the skin,

α_{s_p}: air content of the soil layer deposited on the skin,

n_{s_p}: porosity of the soil layer deposited on the skin.

Furthermore, according to equations 1.1.12 and 1.1.12 **(conditions: soil concentration of pollutant below the limit of solubility, multi-phase equilibrium reached between the different phases of the soil)**,

$$\frac{C_{es\_p}}{C_{s\_p}} = \frac{1}{K_d + \dfrac{\theta_{s\_p}}{MV_{s\_p}} + \dfrac{\alpha_{s\_p} \times H}{MV_{s\_p} \times R \times T_{peau}}} \qquad \text{Equation 2.5.59}$$

and

$$\frac{C_{as\_p}}{C_{s\_p}} = \frac{1}{\dfrac{K_d \times R \times T_{peau}}{H} + \dfrac{\theta_{s\_p} \times R \times T_{peau}}{H \times MV_{s\_p}} + \dfrac{\alpha_{s\_p}}{MV_{s\_p}}} \qquad \text{Equation 2.5.60}$$

We can therefore state:

$$DU_{s\_p} = \frac{1}{K_d + \dfrac{\theta_{s\_p}}{MV_{s\_p}} + \dfrac{\alpha_{s\_p} \times H}{MV_{s\_p} \times R \times T_{peau}}} \times \left(D_e \times \frac{\theta_{s\_p}^{\frac{10}{3}}}{n_{s\_p}^2} + D_a \times \frac{\alpha_{s\_p}^{\frac{10}{3}}}{n_{s\_p}^2} \times \frac{H}{R \times T_{peau}} \right)$$

$$\text{Equation 2.5.61}$$

Symbol	Parameters	Dimensions	Units	Status
DU_{s_p}	Multiphase diffusion coefficient in the soil layer deposited on the skin(expressed relative to the pollutant concentration in the soil)	$M.L^{-1}.T^{-1}$	$kg.m^{-1}.s^{-1}$	C or E
MV_{s_p}	Density of the soil deposited on the skin	$M.L^{-3}$	$kg.m^{-3}$	E
D_a	Diffusion coefficient of the pollutant in air	$L^2.T^{-1}$	$m^2.s^{-1}$	E
D_e	Diffusion coefficient of the pollutant in water	$L^2.T^{-1}$	$m^2.s^{-1}$	E
K_d	Partition coefficient between soil particles and soil water	$L^3.M^{-1}$	$m^3.kg^{-1}$	C or E
θ_{s_p}	Water content of the soil layer deposited on the skin	-	-	E
α_{s_p}	Air content of the soil layer deposited on the skin	-	-	E
n_{s_p}	Porosity of the soil layer deposited on the skin	-	-	C or E
H	Henry constant	$L^2.M.T^{-2}.Mol^{-1}$	$Pa.m^3.mol^{-1}$	C or E
R	Universal gas constant	$L^2.M.T^{-2}.K^{-1}.Mol^{-1}$	$8.31\ J.K^{-1}.mol^{-1}$	I
T_{peau}	Temperature at the surface of the skin	K	K	E

2.5.3.2.2.4. ESTIMATING THE DIFFUSION COEFFICIENT IN THE STRATUM CORNEUM (D_{CC}) AND THE PARTITION COEFFICIENT BETWEEN THE STRATUM CORNEUM AND SOIL (K_{CC_SOL})

Estimating the diffusion coefficient in the skin

In the 1990 publication[12], McKone defines D_{cc} by comparing the stratum corneum to a layer made up of two phases: a liquid phase, and a solid phase representing the dead cells. He also assumes that diffusion of the pollutant in the solid phase is negligible compared to diffusion in the liquid phase, leading to the following statement for the diffusion coefficient in the stratum corneum (D_{cc}):

$$D_{cc} = D_{liq\_cc} \times \frac{C_{liq\_cc}}{C_{cc}} = D_{liq\_cc} \times K_{liqc\_cc}$$

Equation 2.5.62

where C_{liq_cc}: pollutant concentration in the liquid phase of the stratum corneum,

C_{cc}: volume concentration of pollutant in the stratum corneum,

D_{liq_cc}: diffusion coefficient of the pollutant in the liquid phase of the stratum corneum.

The liquid phase is assumed to comprise only water,

hence $K_{liqc\_cc} = \dfrac{C_{liq\_cc}}{C_{cc}} = \dfrac{1}{MV_{cc} \times t_{lip\_cc} \times K_{ow} \times 10^{-3} + \theta_{cc}}$

Equation 2.5.63

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[12] In this article, the equation provided for the transfer coefficient from soil to the skin (K_{sp}) is not as defined in the 1992 article and reproduced here (cf. equation 2.5.55). The expression

provided is equivalent to $K_{sp} = \dfrac{1}{\dfrac{L_{cc}}{D_{cc} \times MV_{s\_p}} + \dfrac{d_{s\_p}}{DU_{s\_p}}}$, which assumes that $\dfrac{C'_{cc}}{C'_{s\_p}} = MV_{s\_p}$,

which is incorrect, in our opinion.

where MV_{cc}: density of the stratum corneum,

t_lip_cc: lipid content of the stratum corneum,

K_{ow}: octanol-water partition coefficient of the pollutant,

θ_{cc}: water content in the stratum corneum.

The diffusion coefficient in the lipid phase is estimated from the Millington and Quirk (1961) relationship:

$$D_{liq\_cc} = \frac{\theta_{cc}^{10/3}}{n_{cc}^{2}} \times D_e$$

Equation 2.5.64

where D_e: diffusion coefficient of the pollutant in water,

n_{cc}: porosity of the stratum corneum.

Assuming the gaseous phase in the stratum corneum to be negligible: $n_{cc} = \theta_{cc}$,

hence $D_{liq\_cc} = \theta_{cc}^{4/3} \times D_e$

Equation 2.5.65

The expression for the diffusion coefficient in the skin given by McKone in the 1990 article is therefore:

$$D_{cc} = \frac{\theta_{cc}^{4/3} \times D_e}{MV_{cc} \times t_{lip\_cc} \times K_{ow} \times 10^{-3} + \theta_{cc}}$$

Equation 2.5.66

Symbol	Parameters	Dimensions	Units	Status
D_{cc}	Diffusion coefficient in the stratum corneum (expressed relative to the volume concentration of pollutant in the skin)	$L^2.T^{-1}$	$m^2.s^{-1}$	C or E
θ_{cc}	Water content in the stratum corneum	-	-	E
D_e	Diffusion coefficient of the pollutant in water	$L^2.T^{-1}$	$m^2.s^{-1}$	E
t_{lip_cc}	Lipid content in the stratum corneum	-	-	E
MV_{cc}	Density of the stratum corneum	$M.L^{-3}$	$kg.m^{-3}$	E
K_{ow}	Octanol-water partition coefficient of the pollutant	$L^3.M^{-1}$	$cm^3.g^{-1}$	E

Comment: the fact of not considering diffusion of the pollutant through lipids very probably tends to underestimate transfer by diffusion into the stratum corneum.

Estimating the partition coefficient between the stratum corneum and soil (K_{cc_sol})

It can be stated:

$$K_{cc\_sol} = \frac{C_{cc}^{'}}{MV_{s\_p} \times C_{s\_p}^{'}} = \frac{C_{cc}^{'}}{C_{es\_p}^{'}} \times \frac{C_{es\_p}^{'}}{MV_{s\_p} \times C_{s\_p}^{'}}$$

Equation 2.5.67

Hence, according to equation 1.1.11,

$$K_{cc\_sol} = K_{cc\_eau} \times \frac{1}{MV_{s\_p} \times K_d + \theta_{s\_p} + \frac{\alpha_{s\_p} \times H}{R \times T_{peau}}}$$

Equation 2.5.68

Symbol	Parameters	Dimensions	Units	Status
K_{cc_sol}	Partition coefficient of the pollutant between the stratum corneum and soil	-	-	C or E
K_{cc_eau}	Partition coefficient of the pollutant between the stratum corneum and water (cf. US EPA 1992 and future documents on the physico-chemical parameters of substances)	-	-	C or E
MV_{s_p}	Density of the soil deposited on the skin	$M.L^{-3}$	$kg.m^{-3}$	E
K_d	Partition coefficient between soil particles and soil water	$L^3.M^{-1}$	$m^3.kg^{-1}$	C or E
θ_{s_p}	Water content of the soil layer deposited on the skin	-	-	E
α_{s_p}	Air content of the soil layer deposited on the skin	-	-	E
H	Henry constant	$L^2.M.T^{-2}.Mol^{-1}$	$Pa.m^3.mol^{-1}$	C or E
R	Universal gas constant	$L^2.M.T^{-2}.K^{-1}.Mol^{-1}$	$8.31 \ J.K^{-1}.mol^{-1}$	I
T_{peau}	Temperature at the surface of the skin	K	K	E

<u>Estimating the product of the diffusion coefficient (D_{cc}) in the skin and the partition coefficient between the stratum corneum and soil ($K_{cc\ sol}$)</u>

The product of D_{cc} and K_{cc_sol} is used in the expression given for mass transfer coefficient from the soil to the skin (equation 2.5.55).

In their 1992 publication, McKone et al. (1992) define the product of D_{cc} and K_{cc_sol} from the dermal permeability coefficient in water ($K_{p,cc}$) and the partition coefficient of the pollutant between soil particles and water (K_d).

The authors consider that, during experiments carried out to measure the dermal permeability coefficient of a pollutant in water, there is a boundary layer between the solution contaminated by the pollutant tested and the skin sample, given the stagnant conditions inherent to this type of test. The measured dermal permeability coefficient ($K_{p,cc}^{mes}$) therefore corresponds to the reciprocal of two resistances, those for the boundary layer at the skin surface and the skin itself:

$$K_{p,cc}^{mes} = \frac{1}{\dfrac{d_e}{D_e} + \dfrac{L_{cc}}{K_{cc\_eau} \times D_{cc}}}$$

Equation 2.5.69

McKone et al. (1992) also established an empirical relationship for $K_{p,cc}^{mes}$ using the experimental measurement of the permeability coefficient for 51 organic substances with molar masses between 18 and 230 g.mol^{-1}. Thus they obtained the following relationship:

$$K_{p,cc}^{mes\,*} = \frac{1}{M^{0,6} \times \left(0,33 + \dfrac{L_{cc}}{2,4.10^{-6} + 3.10^{-5} \times K_{ow}^{0,8}} \right)}$$

Equation 2.5.70

where $K_{p,cc}^{mes\,*}$: dermal permeability coefficient expressed in cm^2.h^{-1}.

By identification between equations 2.5.69 and 2.5.70, they obtained:

$$D_{cc}{}^* = \frac{2,4.10^{-6} + 3.10^{-5} \times K_{ow}^{0,8}}{M^{0,6} \times K_{cc\_eau}}$$ Equation 2.5.71

where $D_{cc}{}^*$: diffusion coefficient in the stratum corneum expressed in cm^2.h^{-1},

or $$D_{cc} = \frac{2,4.10^{-6} + 3.10^{-5} \times K_{ow}^{0,8}}{M^{0,6} \times K_{cc\_eau}} \times \frac{10^{-4}}{3600}$$ Equation 2.5.72

where D_{cc}: diffusion coefficient in the stratum corneum expressed in m^2.s^{-1}.

From equations 2.5.68 and 2.5.72, we can then state:

$$D_{cc} \times MV_{s\_p} \times K_{cc\_sol} = \frac{(2,4.10^{-6} + 3.10^{-5} \times K_{ow}^{0,8}) \times 2,78.10^{-8}}{M^{0,6} \times \left(K_d + \dfrac{\theta_{s\_p}}{MV_{s\_p}} + \dfrac{\alpha_{s\_p} \times H}{MV_{s\_p} \times R \times T_{peau}} \right)}$$ Equation 2.5.73

Symbol	Parameters	Dimensions	Units	Status
D_{cc}	Diffusion coefficient in the stratum corneum (expressed relative to the total volume concentration of pollutant in the skin)	$L^2.T^{-1}$	m^2.s^{-1}	C or E
K_{cc_sol}	Partition coefficient of the pollutant between the stratum corneum and soil	-	-	C or E
M	Molar mass of the pollutant	M.Mol^{-1}	g.mol^{-1}	E
MV_{s_p}	Density of the soil deposited on the skin	M.L^{-3}	kg.m^{-3}	E
K_d	Partition coefficient between soil particles and soil water	$L^3.M^{-1}$	m^3.kg^{-1}	C or E
θ_{s_p}	Water content of the soil layer deposited on the skin	-	-	E
α_{s_p}	Air content of the soil layer deposited on the skin	-	-	E
H	Henry constant	$L^2.M.T^{-2}.Mol^{-1}$	Pa.m^3.mol^{-1}	C or E
R	Universal gas constant	$L^2.M.T^{-2}.K^{-1}.Mol^{-1}$	8.31 J.K^{-1}.mol^{-1}	I
T_{peau}	Temperature at the surface of the skin	K	K	E
K_{ow}	Octanol-water partition coefficient of the pollutant	$L^3.M^{-1}$	cm^3.g^{-1}	E

Comment: the relationship 2.5.73, taken from McKone et al. (1992), is not *a priori* valid for substances with molar masses greater than 230 g.mol^{-1}. Above this, experimental measurements of $K_{p,cc}$ can be used to estimate the product of D_{cc} x K_{cc_sol}. But as equations 2.5.55 and 2.5.69 show, if $K_{p,cc}$ is considered as equal to D_{cc} x K_{cc_eau} / L_{cc}, then the mass transfer coefficient from soil to the skin (K_{ps}) may be underestimated.

2.5.3.2.2.5. LENGTH OF THE DIFFUSION ZONE IN THE SOIL LAYER

In their model, McKone et al. (1992) defined the length of the diffusion path for the pollutant in the soil layer towards the skin, and length of the diffusion path for the pollutant in the soil layer towards the air boundary layer, as equivalent to half the thickness of the soil layer.

The thickness of the soil layer may be defined using the quantity of soil deposited on the skin (Q_{sol_peau}) and the soil density, leading to:

$$d_{s\_p} = \frac{Q_{sol\_peau}}{2 \times MV_{s\_p}}$$

Equation 2.5.74

Symbol	Parameters	Dimensions	Units	Status
d_{s_p}	Length of the diffusion zone in the soil layer	L	m	C or E
Q_{sol_peau}	Soil mass deposited on the skin per unit area (expressed as dry weight)	$M.L^{-2}$	$kg.m^{-2}$	E
MV_{s_p}	Density of the soil deposited on the skin	$M.L^{-3}$	$kg.m^{-3}$	E

Comment: the equations in section 2.5.3.2.2 and the corresponding sub-sections are developed based on the mass concentration of pollutant in the soil, while the equations in McKone (1990) and McKone et al. (1992) are given based on the volume concentration of pollutant in the soil. For this reason, the expressions developed here for the mass transfer coefficient from soil to the skin (K_{sp}), the mass transfer coefficient from soil to the air (K_{sa}) and the multiphase diffusion coefficient in the soil (DU_{s_p}) are identical to the expressions proposed by McKone (1990) and McKone et al. (1992) except for a factor MV_{s_p} (the expressions given above are those from the publications multiplied by the soil density, MV_{s_p}).

2.5.3.2.3. ADVANTAGES AND LIMITATIONS OF APPROACHES BASED ON TRANSFER FLUX

The approach developed in section 2.5.3.2.2 and that presented in the preliminary 1992 US EPA document are not recommended by this organisation and are not reproduced in the document from the 2004 Superfund programme for assessing and managing polluted sites, because the estimates of 'substance partition from soils' are considered to be insufficiently developed.

However, these two approaches, one using the dermal permeability coefficient for the pollutant in soil (K_p^{sol}) and the other using the mass transfer of the pollutant from the soil towards the skin (K_{ps}), have a significant advantage compared to the calculation method based on the absorption rate: K_p^{sol} and K_{ps} remain constant when the quantity of soil deposited on the skin or the concentration in the soil varies, which is not the case for the absorption rate.

Although based on the mathematical representation of transfer by diffusion of the pollutant through the skin, these models only take account of pollutant transfer in the stratum corneum. In contrast to the model developed for exposure from contaminated water, the resistance to transfer associated with the viable epidermis is not considered. This tends to overestimate the pollutant dose effectively absorbed for lipophilic substances.

The phase during which the quantity of pollutant entering the stratum corneum is greater than the quantity leaving it is also not considered. McKone et al. justify this position by:

- the fact that the stratum corneum is less hydrated and therefore thinner when in contact with soil than when in contact with water. McKone et al. consider

that τ_{lag} $(=\dfrac{L_{cc}^2}{6 \times D_{cc}})$ in this case is approximately 1/3 less than the values obtained than for contact with water;

- the fact that contact times with a contaminated soil are generally much longer than when there is contact with contaminated water, as soil particles are assumed to remain on the skin until it is next washed;

- calculation tests have demonstrated that whether or not this period is taken in to account has little effect on the pollutant dose absorbed, estimated for contact times longer than one hour.

McKone recognised that little data existed for dermal absorption from a soil matrix to test these models. Simulations carried out by Bursmater and Maxwell (1991) using the McKone (1990) model give estimates consistent with measurements made by Yang et al. (1989). In this way Bursmater and Maxwell determined, for benzo(a)pyrene, an absorption rate of 2% when 10 mg/cm^2 of contaminated soil was deposited for a contact time of 12 hours, while Yang et al. had measured an *in vivo* absorption rate of 1.1% in rats, after 24 hours exposure, when 10 mg/cm^2 was deposited and an *in vitro* rate of 1.3% on human skin, when 56 mg/cm^2 was deposited for a contact time of 96 hours. However, *in vivo* measurements made by Wester et al. (1990) in rhesus monkeys revealed much higher absorption (average of 13.2% for 40 mg/cm^2 deposited with 24 hours contact). Given the little data available and the variability in that reported, it is currently difficult to reach a conclusion on the effectiveness of these models.

2.5.4. EXPOSURE DOSES ASSOCIATED WITH DERMAL CONTACT

2.5.4.1. CALCULATING INTAKE THROUGH SKIN CONTACT

Intake through skin contact is given by:

$$E_{cc\_ext} = \frac{Q_{pol\_peau} \times A_{exp}}{B_w}$$

Equation 2.5.75

where Q_{pol_peau}: quantity of pollutant in contact with the skin per unit area,

A_{exp}: body area exposed,

B_w: body mass of the receptor.

If contact with the pollutant occurs via soil, the quantity of pollutant in contact with the skin is given by:

$$Q_{pol\_peau} = Q_{sol\_peau} \times C_{s\_p}$$

Equation 2.5.76

where Q_{sol_peau}: quantity of soil on the skin per unit area,

C_s: pollutant concentration in the soil on the skin.

Comments: in the case of swimming in contaminated water, there is currently no agreed method for defining the quantity of pollutant in contact with the skin.

Over the exposure period d_{exp} lasting from T_1 to T_2, the average intake associated with dermal contact with a pollutant is calculated as the average of pollutant doses absorbed from T_1 to T_2. If d_{exp} is broken up into n sub-periods each of duration Δt_i, for which the exposure dose E_{cc_ext} (t_i) can be considered constant, then:

$$\overline{E_{cc\_ext}}(d_{\exp}) = \frac{\sum\limits_{i=T_1}^{T_2} E_{cc\_ext}(t_i) \times \Delta t_i}{T_2 - T_1}$$

Equation 2.5.77

where i: iteration number (number of the sub-period considered) between 1 and n,

and $\sum\limits_{i=1}^{n} \Delta t_i = T_2 - T_1$

Symbol	Parameters	Dimensions	Units	Status
$\overline{E_{cc\_ext}}(d_{\exp})$	Average intake over the exposure duration $d_{\exp}$	M.M^{-1}.T^{-1}	mg.kg^{-1}.j^{-1}	C
$E_{cc\_ext}(t_i)$	Intake through skin contact at time t_i	M.M^{-1}.T^{-1}	mg.kg^{-1}.j^{-1}	C
Δt_i	Period during which the exposure dose equals $E_{cc\_ext}(t_i)$	T	d	E
Q_{pol_peau}	Pollutant mass in contact with the skin per unit area	M.L^{-2}	mg.m^{-2}	E
Q_{sol_peau}	Soil mass deposited on the skin per unit area (expressed as dry weight, consistent with C_{s_p})	M.L^{-2}	kg.m^{-2}	E
C_{s_p}	Pollutant concentration in the soil deposited on the skin	M.M^{-1}	mg.kg^{-1}	C or E
$d_{\exp}$	Duration of the exposure period considered	T	d	C or E
T_1	Beginning of the exposure period	T	d	E
T_2	End of the exposure period	T	d	E
B_w	Body mass of the receptor	M	kg	E
$A_{\exp}$	Body area exposed	L^2	m^2	E

2.5.4.2. CALCULATING THE UPTAKE BY DERMAL CONTACT

The dose absorbed by dermal contact resulting from an exposure event of duration T_{cc}, during which body area $A_{\exp}$ is exposed, is given by:

$$E_{cc\_abs}(T_{cc}) = \frac{DA_{\exp}(T_{cc}) \times A_{\exp}(T_{cc})}{B_w(T_{cc})}$$

Equation 2.5.78

Comment: equations 2.5.17, 2.5.18, 2.5.19, 2.5.20, 2.5.31 and 2.5.42 correspond to the quantities of pollutant absorbed during or after each episode where there is contact with contaminated water or soil. Several body areas can be exposed at the same time under different conditions. In this situation, the products of the quantities of pollutant absorbed by each area multiplied by the area of each of these areas can be added together. Furthermore, if several exposure episodes (interspersed by periods without exposure) occur during the same day, the quantities of pollutant absorbed from each episode must be estimated and added together to obtain the total quantity absorbed for this exposure day.

Over the exposure period $d_{\exp}$ lasting from T_1 to T_2, the average exposure dose by dermal contact is calculated as the average of pollutant doses absorbed from

T_1 to T_2. If d_{exp} is broken up into n sub-periods each of duration Δt_i, for which the uptake E_{cct} ($T_{cc,i}$) can be considered constant, then:

$$\overline{E_{cc\_abs}}(d_{exp}) = \frac{\sum_{i=1}^{n} E_{cc\_abs}(T_{cc,i}) \times \Delta t_i}{T_2 - T_1}$$

Equation 2.5.79

where i: iteration number (number of the sub-period considered) between 1 and n,

and $\sum_{i=1}^{n} \Delta t_i = T_2 - T_1$.

Symbol	Parameters	Dimensions	Units	Status
$\overline{E_{cc\_abs}}(d_{exp})$	Average uptake over the exposure period d_{exp}	$M.M^{-1}.T^{-1}$	$mg.kg^{-1}.j^{-1}$	C
E_{cc_abs} ($T_{cc,i}$)	Uptake by dermal contact for an exposure event of duration T_{cc} taking place at time t_i	$M.M^{-1}.T^{-1}$	$mg.kg^{-1}.j^{-1}$	C
Δt_i	Period during which the exposure dose equals E_{cc_abs} ($t_{cc,i}$)	T	d	E
DA_{exp} (T_{cc})	Pollutant mass absorbed by dermal contact from water and/or soil for a contact time of T_{cc}	$M.L^{-2}$	$mg.m^{-2}$	C or E
d_{exp}	Duration of the exposure period considered	T	d	C or E
T_1	Beginning of the exposure period	T	d	E
T_2	End of the exposure period	T	d	E
$B_w(T_{cc})$	Body mass of the receptor at the time of the exposure event by dermal contact	M	kg	E
$A_{exp}(T_{cc})$	Body area exposed during the dermal exposure event	L^2	m^2	E

3. ESTIMATION OF RISK LEVELS

Risk levels are calculated using exposure levels and corresponding toxicological reference values (VTR) in terms of substance, pathway and exposure duration.

The choice of toxicological reference values goes beyond the scope of this document. For this issue, the reader is referred to existing guides, reports and databases[13].

In certain cases, adjustments can be made to the estimated exposure level, before calculating the risk level, to ensure a better match between the exposure level and the toxicological reference value used. This may be important for estimating, for example, the risk level associated with a baby ingesting breast milk. If the available toxicological value has been defined using adult data (without considering a safety factor for differences in individual sensitivity) and if the pollutant absorption rate in the baby is different to that for the adult, it may be necessary to adjust the baby's exposure dose[14] as follows:

$$\overline{E_{lait\_mat\_eq}}(d_{\exp\_nour}) = \frac{\overline{E_{lait\_mat}}(d_{\exp\_nour}) \times t_{abs\_nour}}{t_{abs\_adulte}}$$

Equation 3.1

where $\overline{E_{lait\_mat\_eq}}(d_{\exp\_nour})$: baby's adjusted exposure dose,

$\overline{E_{lait\_mat}}(d_{\exp\_nour})$: average exposure dose by ingested by the baby via breast milk over the exposure period $d_{\exp\_nour}$,

t_{abs_nour}: absorption rate of the pollutant by the baby,

t_{abs_adulte}: absorption rate of the pollutant by the adult.

These practices, which are not always done, should always be based on an assessment of the available toxicological data.

The calculation for the risk level is presented below. It is slightly different depending on the type of effect considered (threshold effect or effect without threshold).

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[13] It is worth noting that there are currently few toxicological values relating to the dermal exposure pathway. To estimate the risk associated with the pollutant dose absorbed after dermal contact with a contaminated soil or water, in the absence of such values the US EPA (1989) recommends using toxicological values defined for the oral pathway, after adjusting those related to the oral absorption rate. In reality, the toxicity of a substance depends on biological mechanisms involved after its administration, which may be different depending on the exposure route. Unlike the US EPA, the French Department of Health, in its circular 2006-234 dated 30/05/06, asks the decentralised services in charge to give an opinion on the health effects of projects arising from an impact study, to ensure that petitioners do not transpose any available Toxicological Reference Value for ingestion or inhalation to the dermal exposure route.

[14] This approach is used by the US EPA (1998) to estimate exposure of the baby to dioxins through ingesting breast milk.

3.1. CALCULATING THE RISK LEVEL FOR THRESHOLD EFFECTS

For threshold effects, a danger quotient is first calculated for each pathway and each substance.

For the inhalation or respiratory pathway, the danger quotient (QD) is given by:

$$QD = \frac{\overline{C_{inh}}(d_{exp})}{VTR}$$

Equation 3.1.1

with the Toxicological Value (VTR) expressed in terms of concentration.

For the ingestion (or oral) and dermal pathway, the danger quotient (QD) is given by:

$$QD = \frac{\overline{E}(d_{exp})}{VTR}$$

Equation 3.1.2

with the Toxicological Reference Value (VTR) expressed in terms of dose.

and $$\overline{E}(d_{exp}) = \sum_{j} \overline{E_j}(d_{exp})$$

Equation 3.1.3

where $\overline{E_j}(d_{exp})$: oral exposure dose associated with vector j, averaged over the exposure period d_{exp}

In equations 3.1.1 to 3.1.3, the exposure duration d_{exp} used depends on the type of effect considered. It may be an acute effect associated with short-term exposure (from a few seconds to a few days), sub-chronic effects (for exposure durations from a few days to a year) or chronic effects (for exposure from a year to whole life). Thus, d_{exp} should correspond to the shortest duration for which the effect studied can be expressed. If the exposure level varies with time, the risk level should then be assessed over an exposure duration d_{exp} where the inhaled concentration or exposure dose is the greatest.

For a polluted site that is no longer operating (no inflow but loss of pollutant over time), the highest exposure occurs at the beginning of the exposure period considered. Unlike the case of an operational facility (and in the absence of other sources), if pollutant emissions and exposure conditions are constant over time, the highest exposure is obtained at the end of the emission period. In simplified form, given the uncertainties (over the actual operational period of the facility, the continuous and constant nature of the emissions, etc.), the exposure level used to estimate non-carcinogenic chronic risk is sometimes calculated at time t where exposure is at its greatest, and not over an entire year.

Symbol	Parameters	Dimensions	Units	Status
QD	Danger Quotient	-	-	C
$\overline{C_{inh}}(d_{exp})$	Average concentration inhaled over the exposure period d_{exp}	M.L^{-3}	mg.m^{-3}	C
$\overline{E}(d_{exp})$	Oral or dermal exposure dose associated with different vectors, averaged over exposure period d_{exp}	M.M^{-1}.T^{-1}	mg.kg^{-1}.d^{-1}	C
$\overline{E_j}(d_{exp})$	Oral exposure dose associated with vector j, averaged over the exposure period d_{exp}	M.M^{-1}.T^{-1}	mg.kg^{-1}.d^{-1}	C
VTR	Toxicological reference value (expressed in terms of concentration for the inhalation pathway and in terms of dose for oral and dermal pathways).	M.L^{-3} or M.M^{-1}.T^{-1}	mg.m^{-3} or mg.kg^{-1}.d^{-1}	E

Regarding addition of risk factors, the general rule is to add danger quotients for substances causing the same effect on the same organ by the same biological mechanism. For more information about these rules and usual practices, the reader should also refer to existing guides, reports and circulars.

3.2. CALCULATING THE RISK LEVEL FOR EFFECTS WITHOUT THRESHOLD

For effects without threshold, the calculated risk level is the probability for an individual of developing the effect associated with the substance. For carcinogenic substances where the effect is considered without threshold, this probability is calculated over the whole life. In this way, exposure levels are reported for whole life.

For the inhalation or respiratory pathway, the individual lifetime cancer risk (RI) is given by:

$$RI = \frac{\overline{C_{inh}}(d_{exp}) \times d_{exp}}{T_m} \times VTR \qquad \text{Equation 3.2.1}$$

For the ingestion (or oral) and dermal pathway, the individual lifetime cancer risk is given by:

$$RI = \frac{\overline{E}(d_{exp}) \times d_{exp}}{T_m} \times VTR \qquad \text{Equation 3.2.2}$$

Ref: DRC-14-141968-04378A

Symbol	Parameters	Dimensions	Units	Status
RI	Individual lifetime cancer risk	-	-	C
$\overline{C_{inh}}(d_{exp})$	Average concentration inhaled over the exposure period d_{exp}	$M.L^{-3}$	$mg.m^{-3}$	C
$\overline{E}(d_{exp})$	Oral or dermal exposure dose associated with different vectors, averaged over exposure period d_{exp} (cf. equation 3.1.3)	$M.M^{-1}.T^{-1}$	$mg.kg^{-1}.d^{-1}$	C
d_{exp}	Total exposure duration	C	d	E
T_m	Period of time over which exposure is reported. For carcinogenic substances, a period of 70 years is conventionally considered	C	d	I
VTR	Toxicological reference value, called cancer slope factor (corresponding to the inverse of a concentration for the inhalation pathway and the inverse of a dose for oral and dermal pathways)	$(M.L^{-3})^{-1}$ or $(M.M^{-1}.T^{-1})^{-1}$	$(mg.m^{-3})^{-1}$ or $(mg.kg^{-1}.d^{-1})^{-1}$	E

An overall lifetime cancer risk is then calculated by summing the individual lifetime cancer risks associated with the different carcinogenic substances without effect threshold, the different exposure pathways and different exposure durations.

This calculation is an approximation, because it does not take account of the combined probability for an individual of developing cancer due to exposure to several pollutants. This approximation remains valid for low individual lifetime cancer risks (<0.01).

Comment: In the case of a study relating to a given contamination source, we talk about excess individual lifetime cancer risk (from the exposure level attributable to this source), represented by the abbreviation ERI, which is the additional probability for an individual of developing a carcinogenic effect due to this source compared to the background exposure.

4. DISTINCTION BETWEEN CONCENTRATIONS, DOSES, RISKS ATTRIBUTABLE TO ONE OR MORE CONTAMINATION SOURCES AND TOTAL CONCENTRATIONS, DOSES AND RISKS

Depending on the study objectives, the risk assessor may seek to estimate concentrations in the media, exposure levels and risk levels attributable to a specific source or the total concentrations, exposure levels and risk levels to which individuals are subjected.

In this way, for a health risk assessment conducted as part of an impact study, we seek to define the concentrations, exposure levels and risk levels attributable to emissions from the facility studied. But it may also be necessary to calculate the total concentrations, exposure levels and risk levels, to estimate the proportion of these indicators attributable to this facility. Total concentrations and exposure levels can also be calculated to compare them with measured data.

All the concentrations presented above apply to calculating concentrations, exposure levels and risks attributable to one or more contamination sources. These equations can also be used to calculate total concentrations, exposure levels and risk levels. However, total concentrations in environmental media, such as the soil, air, groundwater and surface water, are not calculated directly from the equations in section 1. They are actually calculated as the sum of concentrations attributable to local sources (estimated using the equations in section 1) and background concentrations.

As an example, consider a study relating to atmospheric emissions from a chimney:

- the soil concentration attributable to the facility will be calculated using atmospheric deposition of pollutant due to emissions from the chimney;

- the pollutant concentration in plants attributable to the facility will be calculated using the pollutant concentration in the soil (estimated as shown above, without taking account of the background concentration), particle deposits and the pollutant concentration in the air attributable to the facility;

- exposure levels and exposure risks attributable to the facility will be calculated using the concentrations attributable to the facility in the different exposure media.

- total pollutant concentrations in plant-derived products will be calculated using the transfer equations presented in section 1.6 and total pollutant concentrations in the air, soil and perhaps water;

- exposure levels and total risks will be calculated from total concentrations in the different exposure media of the individuals (soil, air, plant and animal products).

  The indicators thus obtained will correspond to the total exposure and risk levels associated with the site or impact zone for the contamination source studied. By adding to these results the exposure and risk levels associated with exposure vectors located outside the site or impact zone for the contamination source studied (such as foodstuffs consumed but produced

outside this zone), we will obtain the total exposure and risk levels, respectively, to which individuals are subjected.

On the other hand, pollutant concentrations in the soil, outdoor air, indoor air and groundwater or surface water attributable to the facility must be calculated using the equations described in sections 1.1 to 1.5 and concentrations attributable to this facility in the inflow media. To the attributable pollutant concentrations, thus obtained in the soil, outdoor air, etc., we will then add the pollutant concentrations in these media associated with the background concentration.

In the previous example, for atmospheric emissions from a chimney, the calculation of total pollutant concentration in the soil requires estimating the concentration in the soil due to atmospheric fallout from the chimney, and adding the background concentration in the soil to it. In fact, taking account of total atmospheric deposition on the soil, including deposition associated with ubiquitous sources, would not enable us to know the total pollutant concentration in the soil, and adding the background concentration in the soil to the concentration calculated using total deposits on the soil would result in counting the background concentration in the soil attributable to the background concentration in the air twice.

Even if total pollutant concentration in an upstream medium and a downstream medium should be considered to estimate the quantity of pollutant going from one medium to the other by convective or diffusive transport, the approach described here has been selected because the mobility of a chemical compound can vary according to its origin (geochemical, made-made, etc.) or the age of the contamination. Yes, it is difficult over a site to have differentiated information on the mobility of different contamination sources and to take account of them when performing a total mass balance of chemical substances. With the selected approach, it will be noted that the proportion of pollutant attributable to the studied source lost by a medium can be overestimated, because the proportion of pollutant associated with the background concentration can contribute to transfers, while the total mobility of a substance is limited by its vapour pressure and solubility. However, this overestimated component should be considered in relation to the uncertainties associated with assuming an instantaneous equilibrium between the different phases of a medium or the definition of partition coefficients for the substance between solid and liquid phase. In addition, loss phenomena in classical ERS are generally only taken into account to analyse uncertainties and the scale of possible variations on the results.

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APPENDIX: MATRIX OF INTERACTIONS BETWEEN DIFFERENT MEDIA (ALL TRANSFER MECHANISMS AND EXPOSURE PATHWAYS TO HUMAN)

Soil Degradation Sorption	Diffusion Evaporation Resuspension of particles	Convection Diffusion	Leaching	Runoff Erosion		Direct uptake from the soil Rainsplash	Ingestion	Ingestion Dermal absorption
Particulate and gaseous deposition	Outdoor air Dispersion Degradation	Convection Diffusion		Particulate and gaseous deposition		Particulate deposition Foliar absorption of gaseous pollutant		Inhalation of gases and particles
	Convection Diffusion	Indoor air Degradation						Inhalation of gases and particles
Irrigation Fluctuation of water table	Evaporation Diffusion	Evaporation Convection Diffusion	Groundwater Dispersion Degradation Sorption	Drainage of groundwater		Irrigation	Ingestion	Ingestion Dermal absorption
Irrigation	Volatilisation		Refilling of groundwater	Surface water Dispersion Degradation Sorption	Sedimentation Diffusion	Irrigation	Ingestion Bioconcentration Bioaccumulation	Ingestion Dermal absorption
				Resuspension Diffusion	Sediments Degradation Sorption		Bioaccumulation	Dermal absorption
Decomposition						Plants Degradation	Ingestion	Ingestion
Decomposition							Animals	Ingestion
								Humans Ingestion of breast milk