TNO Environment, Energy and Process Innovation

Laan van Westenenk 501
Postbus 342
7300 AH Apeldoorn
The Netherlands

www.mep.tno.nl

T +31 55 549 34 93
F +31 55 541 98 37
info@mep.tno.nl

TNO-report

R 98/376

Manual for performing risk assessments for persistent organic pollutants in aquatic ecosystems

Guidelines for critical limits, calculation methods and input data

Date 17 November 1998

Authors
D.J. Bakker [1)]
W. de Vries [2)]
E.J. van de Plassche [3)]
W.A.J. van Pul [3)]

[1)] TNO Institute of Environmental Sciences, Energy Research and Process Innovation, Den Helder, The Netherlands
[2)] DLO Winand Staring Centre, Wageningen, The Netherlands
[3)] National Institute of Public Health and the Environment, Bilthoven, The Netherlands

Order no. 27595

Keywords
- calculation method
- critical limit
- environmental risk assessment
- persistent organic pollutant

Intended for
Ministry of Housing, Spatial Planning and the Environment
Directorate-General for Environmental Protection
P.O. Box 30945
2500 GX The Hague
The Netherlands

Preface

The present production and use of Persistent Organic Pollutants (POPs) are leading to emission of these compounds to the environment. The emitted POPs are prone to atmospheric transport and deposition. To make adequate environmental policies concerning a reduction of the emission of POPs, the effects and the risks resulting from the deposition of POPs should be estimated. With the wish to support the development of risk analysis for POPs, the Dutch Ministry of Housing, Spatial Planning and the Environment has sponsored the edition of two manuals: this manual for POPs in terrestrial ecosystems and another one for POPs in aquatic ecosystems. The manuals have been developed in accordance with the results and recommendations of the recently held "International Workshop on Critical Limits and Effect-Based Approaches for Heavy Metals and POPs" in Bad Harzburg, Germany, in 1997, within the framework of the United Nations Economic Commission for Europe's Convention on Long-range Transboundary Air Pollution (UN/ECE CLRTAP).

The development towards these manuals started in 1994. In 1995 and 1996, first drafts were presented at the sixth and seventh workshop of the Co-ordination Centre for Effects (CCE) under the auspices of the Convention. Taking the recommendations from these workshops into account the first preliminary manuals were published in 1996. After thorough discussions at the ninth CCE workshop in 1997 and at the "International Workshop on Critical Limits and Effect-Based Approaches for Heavy Metals and POPs" the preliminary manuals have been further developed. During the development of methodologies on effects-based approaches for POPs, it became clear that a critical loads approach for POPs similar to the one in use for acidifying air pollutants, was not considered appropriate. Alternatively, as a procedure to be favoured with respect to UN-ECE Protocols, it was recommended that risk assessment methods for POP should be developed.

The manuals as they now appear show how critical limits can be derived and how risk assessment for POPs in ecosystems can be performed according to present scientific understanding. Through careful reviews, methods were selected and presented including methodologies demonstrating the source-receptor linkage. Where necessary, methodologies were newly developed. The approaches described may be applied with the character of a pilot study until further international agreement is reached on an LTN-ECE-wide common procedure. Hopefully, this manuals will provide a valuable tool for those who wish to perform risk assessment for POPs in terrestrial ecosystems. Eventually, such risk assessment might form a basis for adding POPs to the existing POP Protocol under the Convention or for evaluating measures for POPs already decided upon in this Protocol.

Heinz D. Gregor
Chairman of the Task Force on Mapping Critical Loads and Levels
UN/ECE CLRTAP

Contents

Acknowledgements

We thankfully acknowledge the contributions of many colleagues who have supplied us with useful comments and suggestions on previous (draft) versions of this manual. We further thank all those who took part in the fruitful discussions during the sixth (1995), seventh (1996), eighth (1997) and ninth (1998) CCE workshops in Helsinki, Budapest, Galway and Kristiansand respectively and during the Bad Harzburg workshop (1997).

Summary

In this manual several methods (models) are presented that can be used to assess the risks of persistent organic pollutants (POPs) in aquatic ecosystems. All models assume that the risk assessment is performed for 'indicator ecosystems', which are more or less complete aquatic ecosystems of limited size, such as inland lakes. As most lakes are however not isolated hydrological units, the catchment that drains into the lake is also taken into account. The indicator ecosystems can be selected as the most representative, the most vulnerable, the most 'suspect' or the most interesting in a region or country. Two main approaches for risk assessment are presented of which the final results are equal but that take a different starting point. The first (PEC:PNEC) approach takes the actual load of the POP on the selected ecosystem as a starting point, calculates the Predicted Environmental Concentration (PEC) in the water and/or sediment and compares this with a critical limit, such as the Predicted No Effect Concentration (PNEC). The second (AL:ML) approach takes the critical limit (concentration) as a starting point, calculates the effect-based maximum load (ML) and compares this with the actual load (AL). For both approaches, a scheme is presented that the reader can use to find his or her way through the manual to prepare and perform a risk assessment. Within both approaches, a distinction is made between simple models with relatively low data requirements and more elaborated models with higher data requirements. The input data that are required for the various models are discussed in a separate chapter of this manual. All models are based on a steady-state mass balance equation, which takes into account the most relevant input and output fluxes of the POP into and out of the aquatic system. The models are furthermore based on the concept of equilibrium partitioning between the different phases in the aquatic system. Other assumptions are that the water and top sediment are homogeneously mixed.

The choice of critical limit, which is used either as PNEC or as the basis for the effect-based maximum load (ML), is very important in risk assessment. Therefore, this manual also presents models to derive critical limits for various receptors. Since many POPs have the potential to bioaccumulate and/or biomagnify in food chains or food webs, the models presented are not restricted to lower aquatic organisms such as water flee and small fish but also include (top-)predators such as larger fish and fish-eating birds and mammals. Humans that consume fish or water from the aquatic system of concern are also considered. Again, both simple models with low data requirements and more detailed models with higher data requirements are presented. All models to derive critical limits have been described in a way that the resulting critical limit is expressed in a critical concentration in the water or top sediment. In this way, the models to calculate the PEC or the ML can be used, without adjustment, with critical limits for different receptors. Critical limits for POPs that are in use with the UN-ECE countries are presented in an annex.

The manual further includes chapters on determining the actual POP load by modelling atmospheric transport and deposition and on the uncertainties

associated with the different parts of the risk assessment methods. And although the manual focuses on atmospheric deposition of POPs, the risk assessment methods presented in this manual are based on total loads and are therefore also suitable for the assessment of other (non-atmospheric) loads. For some POPs the non-atmospheric routes of contamination are equally or even more important than atmospheric deposition.

1. Introduction

In this chapter the background and aim of this manual are discussed. Furthermore, the reader is given a guideline on how to use the manual for performing risk assessments for persistent organic pollutants (POPs) in aquatic ecosystems.

1.1 Background and aim

There is a growing international concern on the long-range atmospheric dispersion of POPs and on their impact on the environment. As a result of this, many working groups and task forces work on policies to deal with this problem (Sliggers and Jager, 1993). Many of these working groups have been established under international organisations, such as ministerial conferences (North Sea, Rhine, Arctic), the Oslo, Paris and Helsinki Commissions, the United Nations Economic Commission for Europe (UN-ECE) and the European Union (EU). Most groups are working on emission reduction programmes but others are concerned with monitoring programs, emission inventories and state-of-the-environment surveys.
At this moment, effect-based approaches for abatement of POP emissions under the UN-ECE Convention of Long Range Transboundary Air Pollution (UN-ECE CLRTAP) are not considered feasible yet. Therefore the control, reduction and elimination of discharges, emissions and losses of POPs, as described in the recently signed POP protocol, are based on the precautionary principle and best available techniques. This means that, although POPs in the protocol are selected on the basis of their toxicity, persistence, bioaccumulation, long range atmospheric transport and likeliness to cause significant adverse effects on human health and the environment, differences in susceptibility of receptors to the POP input are not taken into account in defining the technical abatement measures. There is however a general believe that risk assessment methods can and should be used to assess the risks of POPs in the environment and that they could be used to determine which POPs should be added to the protocol. The aim of this manual is to present guidelines for performing risk assessments for POPs in aquatic ecosystems, on the basis of various criteria and methods. The implicit aim of this manual is to serve as a next step in reaching international agreement within the UN-ECE countries on both the methods and the critical limits to be used in such risk assessment.

The general approach for the risk assessment scheme in this manual is mainly based on the approach that was followed in a risk assessment study for surface waters in the Netherlands (the ATMODEP study; Bakker, 1995). It is further partly based on methods developed earlier within the framework of the ESQUAD study 'The Impact of Atmospheric Deposition of Non-Acidifying Pollutants on the Quality of European Forest Soils and the North Sea' (Van den Hout, 1994; Van den Hout *et al.*, 1998; Van Jaarsveld, 1994; Van Pagee and Villars, 1994), in which a first attempt was

made to establish direct relationships between atmospheric deposition of POPs and the possible exceedance of critical limits on a European scale.
The first draft of this manual was presented at the sixth workshop of the Coordination Centre for Effects (CCE), under the auspices of the UN-ECE CLRTAP, in Helsinki, Finland in April 1995. As a result of the comments that were given at this workshop, both simplified and elaborated approaches were introduced in the second draft of the manual. The second draft (Bakker and De Vries, 1996) was presented at the seventh CCE workshop in Budapest, Hungary in March 1996 as a preliminary manual. At the eighth CCE workshop in Galway, Ireland in April 1997, the methods in the preliminary manual were further discussed. In November 1997, the preliminary manual was used as the basis for a background document for the International Workshop on Critical Limits and Effect Based Approaches for Heavy Metals and Persistent Organic Pollutants, held in Bad Harzburg, Germany (Bakker and De Vries, 1998).
Until the Bad Harzburg workshop, the methods in the draft manuals and background document were directed at calculating critical loads for POPs, similar to critical loads for acidifying substances. From the Bad Harzburg workshop it became however clear that there is not yet international consensus on the necessity and/or possibility of calculating critical loads for POPs. Main objections against calculating critical loads for international emission abatement purposes, were the believe that for many POPs reliable source-receptor relations are difficult to establish and the opinion that meaningful European scale mapping of critical loads and their exceedances is not yet feasible for POPs due to lack of data and large associated uncertainties. It was however also concluded at the workshop that effort should be undertaken to further develop risk assessment methods for POPs. It was therefore decided that a next manual would have the character of a manual for performing risk assessments for POPs in 'indicator ecosystems', in which mapping on a national or international scale is not considered a goal.
Further comments from the Bad Harzburg workshop with respect to the methods in the previous manual were related to the fact that essential key receptors, *i.e.* top-predators and human beings, were not taken into account in the method, although it is known that POPs have the potential to bioaccumulate and biomagnify. It was therefore decided to extend the method in the manual with the processes of bioaccumulation and biomagnification. At the ninth CCE workshop in Kristiansand in May 1998 these improvements of the methodology were proposed and discussed. The proposed changes have been implemented in the underlying version of the manual, which therefore reflects the outcome of the latest discussions.
The latest changes to the manual were the addition of a chapter on determining the actual load of POPs with a special focus on atmospheric transport modelling of POPs, in order to demonstrate the possibilities and impossibilities of establishing the source-receptor relation of POPs with current state-of-the-art atmospheric models and the extension of the risk assessment models to include the catchment area of the aquatic ecosystem of concern.

1.2 Guideline for the use of this manual.

In risk assessments one can distinguish between effect assessment and exposure assessment. With effect assessment one determines the type and magnitude of the response of a receptor to the exposure to a pollutant. With exposure assessment one determines the dose or concentration to which the receptor is exposed.
In this manual, two modelling approaches for local risk assessment for POPs in aquatic ecosystems are presented. The first (PEC:PNEC) approach takes the actual load of the POP on the selected ecosystem as a starting point, the second (AL:ML) approach takes the critical limit (concentration) as a starting point.

PEC:PNEC approach
In this approach, the Predicted Environmental Concentration (PEC) that results from the actual load on the aquatic ecosystem is calculated. Here exposure assessment includes the translation from load on the water and catchment area to concentrations in the water and sediment. The calculated PECs are subsequently compared with the critical limits in the aquatic ecosystem, which are the Predicted No Effect Concentration (PNEC). The ratio PEC:PNEC gives an indication of the risk that the ecosystem suffers from the actual load of the POP. If the ratio is greater than 1, negative effects on the receptor are predicted, if it is smaller than 1, no negative effects are predicted.

AL:ML approach
In this approach an effect-based maximum load (ML) is calculated for the aquatic ecosystem and the catchment area on the basis of the critical limit in the aquatic ecosystem. Here effect assessment is combined with part of the exposure assessment (the part within the aquatic system). The calculated effect-based maximum load is subsequently compared with the actual load (AL). Exposure assessment here solely consists of determining the actual load on the aquatic ecosystem and catchment area. The ratio AL:ML gives an indication of the risk that the ecosystem suffers from the actual load of the POP. If the ratio is greater than 1, negative effects on the receptor are predicted, if it is smaller than 1, no negative effects are predicted.

The 'PEC:PNEC' approach is the approach usually applied in risk assessment methods. The 'AL:ML' approach is based on the same model as used in the PEC:PNEC approach but it is used 'in reversed order'. As the ratios PEC:PNEC and AL:ML are identical, it makes in principal no difference which method is used for the risk assessment. The advantage of the 'AL:ML' approach is that one can start the calculations without having the information on the actual load. As soon as this information becomes available from measurements or model calculations one can do the comparison between AL and ML. The advantage of the PEC:PNEC approach is that one can start the calculations without having to choose the critical limit. As soon as this limit is chosen one can do the comparison between PEC and PNEC.

In this manual both approaches are presented and the different steps in both approaches are shown in Figure 1.1. The reader can use this figure to determine his or her way through the manual, going from one indicated chapter to the next in the process of preparing and performing the risk assessment.

AL:ML approach	***PEC:PNEC approach***
1. Select a receptor (Chapter 2)	1. Select a receptor (Chapter 2)
↓	↓
2. Determine the critical limit (PNEC) (Chapter 4)	2. Determine the actual load (AL) (Chapter 3)
↓	↓
3. Select a computation method (model) (Chapter 5)	3. Select a computation method (model) (Chapter 5)
↓	↓
4. Collect the input data (Chapter 6)	4. Collect the input data (Chapter 6)
↓	↓
5. Calculate the effect-based maximum load (ML) (Chapter 5)	5. Calculate the Predicted Environmental Concentration (PEC) (Chapter 5)
↓	↓
6. Determine the actual load (AL) (Chapter 3)	6. Determine the critical limit (PNEC) (Chapter 4)
↓	↓
7. Determine the AL:ML ratio	7. Determine the PEC:PNEC ratio

Figure 1.1 Flow chart for risk assessment using this manual. The approach on the left is the effect-based maximum loads (AL:ML) approach, the approach on the right is the PEC:PNEC approach.

2. Selecting a receptor

Selecting a receptor is the first step in the risk assessment schemes presented in figure 1.1 in paragraph 1.2. This is the case in both the PEC:PNEC approach and the AL:ML approach.
When selecting a receptor for risk assessment purposes, the crucial question is: 'What do we want to protect?'. In aquatic ecosystems this can be the organisms lower in the food chain such as water flee and small fish but also (top-)predators such as larger fish, fish-eating birds and mammals and human beings that use the surface water for drinking water or that consume fish from the aquatic ecosystem.
In an earlier stage of development of the manual emphasis was laid on the protection of aquatic organisms that are subject to a more or less direct impact of the polluting substance. This meant that the risk assessment was directed at the lower aquatic organisms. Organisms higher in the food chain were not considered. From the discussions at the Bad Harzburg workshop it became however clear that the general opinion was that, due to the bioaccumulating and biomagnifying nature of many POPs, the risk assessment should be primarily directed at (top-)predators, including humans, but without neglecting lower organisms.
As a result of this, the methods presented in this manual are meant to be applied on more or less complete aquatic ecosystems. These ecosystems should be of limited size to prevent that the data requirements become too large. A single ecosystem can be defined in much more detail than larger areas and if desired, measured values of certain input data can replace estimated or assumed values. Therefore, the approach is assumed to be applied to inland lakes. As most lakes are however not isolated hydrological units, the catchment that drains into the lake is also taken into account. Application on a national scale can take form by defining 'indicator ecosystems' for the country. These indicator ecosystems can be chosen as the most representative for the country, as the most vulnerable ones of the country or as the ecosystems of special interest or suspicion in the country. Both abiotic conditions (*e.g.* water, sediment and catchment characteristics) and biotic conditions (type of organisms present, foodchains *etc.*) play a role in choosing the indicator ecosystems of the country. Ecological maps and associated maps may help in defining the countries' indicator ecosystems. On a European scale it is also possible to define indicator ecosystems, either by taking the national indicator ecosystems or by defining indicator ecosystems representative for parts of Europe.

3. Determining the actual load of POPs

3.1 Introduction

Determining the actual load of a POP on the indicator ecosystem (including the catchment area) is the second step in the PEC:PNEC risk assessment scheme presented in figure 1.1 in paragraph 1.2. In the case of the AL:ML approach, it is the second last step.
The actual load of a POP on an aquatic ecosystem can have two forms: Direct and indirect loads. Direct loads are for example atmospheric deposition on the surface of the lake and other direct loads due to emissions from *e.g.* ships, households and industry. Indirect loads are loads that reach the lake via the incoming water and may be the result of atmospheric deposition or other loads on the catchment area, from which it may reach the lake after leaching and/or surface runoff . Both direct and indirect loads can be determined by means of measurements or by means of model calculations. As measurement techniques are beyond the scope of this manual and calculating direct other loads is generally rather straightforward, these subjects are not discussed in this manual. The discussion in this chapter is therefore directed at modelling atmospheric transport and deposition of POPs and at establishing source-receptor relationships for POPs. The source-receptor relationship represents the link between emission and atmospheric deposition and reveals which emissions are responsible for the actual load on the ecosystem of concern. Having established the source-receptor relationship, one can determine where abatement measures are most effective if the PEC:PNEC or AL:ML ratio indicates that the actual load imposes an unacceptable risk to the ecosystem.
In order to demonstrate the possibilities and impossibilities of modelling atmospheric transport and deposition of POPs, the next paragraphs are dedicated to establishing the source-receptor relationship for POPs.

3.2 Source-receptor relationships for POPs

The main difficulty in establishing the source-receptor relationship for POPs is the possibility that (semi-)volatile (gaseous) POPs can re-volatilise after being deposited on the earth's surface. One should however bear in mind that for a large number of POP like dioxins and PAHs this re-volatilisation is not a major process. For those substances the source-receptor modelling as developed for acidifying compounds and heavy metals can be used. Therefore, before starting modelling transport and deposition of a POP, the POP should be screened on its atmospheric behaviour (removal processes) defined by its physicochemical properties. Subsequently it can be concluded whether it has a large re-volatilisation potential or not. A screening method for this atmospheric behaviour is given by Van Pul *et al.* (1998).

If a POP has re-volatilisation potential, this has two implications. The first is the fact that the POP can be transported over longer distances than its first site of deposition suggests because it can live through several 'cycles' of deposition and re-volatilisation. Re-volatilisation can only occur when the atmospheric concentration of the POP drops below the atmospheric concentration with which the water, soil or vegetation is in equilibrium at that moment. The second implication, which is in fact an extension of the first, is the fact that certain areas may have build up relatively high water or soil concentrations during several decades of historic air pollution and can at present (with lower atmospheric concentrations) perform as permanent emission sources. These two implications will be discussed in the next two paragraphs.

3.3 Modelling atmospheric transport of (semi)-volatile POPs

An overview of the modelling of transport and deposition of POPs on a European scale was presented at the Bad Harzburg International Workshop on Critical Limits and Effect-based Approaches for Heavy Metals and POPs (Dutchak *et al.*, 1998). The transport and dispersion of POPs in the atmosphere are similar as for other air pollution components. Therefore existing models, which were originally developed in other air pollution fields like in acidification and ozone problems, can be used to describe the transport processes for POPs. These models have however to be adjusted to describe the removal of POPs from the atmosphere. Particularly the exchange of gaseous POPs at the soil and sea surfaces has to be modelled in more detail since this process is dependent on the amount of POP already present in the receiving surface. The EMEP/MSC-E -ASIMD and the RIVM-EUROS transport models have been extended with soil and sea compartment modules with which the dynamic exchange of gaseous POPs is calculated (Pekar, 1996; Jacobs and Van Pul, 1996). The soil module consist of five soil layers in which POP behaviour is described with linear partitioning theory and which is based on Jury *et al.(*1983). In the water compartment the exchange between atmosphere and water is assumed to take place according to the theory of Liss and Slater (1974). The modules are described in detail by Jacobs and Van Pul (1996). So, with the extended ASIMD and EUROS models the deposition as well as the re-volatilisation of substances can be calculated. The deposition of a POP received by a surface is now the difference between the deposition and re-emission fluxes or in other words a net-deposition. In Jacobs and Van Pul (1996) and MSC-E progress report (MSC-E, 1997) examples of the net-deposition of lindane and PCB-153 using the UBA/TNO (Berdowski *et al.*, 1997) emission data base were presented. It should be stressed that these calculations are first attempts to explain environmental levels of these substances by using an emission-based modelling approach. The uncertainty in the calculations is typically a factor of 3 and largely due to the uncertainty in emissions. Nevertheless, with the emission-based modelling approach, the relationship is established between the sources and the (net-)deposition of a POP taking into account the re-volatilisation.

Constructing single source-receptor relationships *i.e.* between one source (area) and one receptor (area), is not simple due to the possible re-volatilisation of the substance and makes this relationship a function of in principle all sources in the modelled area as well. A possible way to establish these relationships is to start with the present emission distribution over Europe and make small variations (typically 10%) in these emissions country by country. The contribution of the emissions of a country to the net-deposition in another country is then found in a situation that is close to the existing equilibrium situation, with respect to the exchange of the POP. In this way a first order country to country contribution matrix will be obtained. However, this method is under development and should be elaborated in the near future.
Single source-receptor relationships are however not absolutely necessary for obtaining future emission targets. Another way, for instance, is to define emission scenario's for the entire area of interest and run the model. In this very straightforward way, the gap between the calculated actual loads (AL) and the effect-based maximum loads (ML) is found by "trial and error". The latter method certainly needs some computing time but is not expected to be more time consuming than the first. Moreover, computing power is still increasing and will not be a bottleneck to apply the above methods.

3.4 Dealing with re-volatilisation of historic pollution

Re-volatilisation of historic pollution which has accumulated over several decades is in essence not much different from the re-volatilisation discussed in the previous paragraph. The main difference is that in the case of historic pollution it is assumed that re-volatilisation from the soil or water is a more or less continuous process (*i.e.* the present atmospheric concentration is continuously lower than the atmospheric concentration that would be in equilibrium with the present soil pollution).
Re-volatilisation of historic pollution is only important for persistent organic compounds which have a very small degradation rate in soil or water (otherwise they would not accumulate to form an important source) and do have a specific potential to evaporate (if this potential is too high, the source would not last very long; if the potential is too low, the source strength would not have much significance). The group of POPs for which re-volatilisation of historic pollution plays an important role is therefore limited.
There are two ways to deal with historic pollution in the present modelling tools. The first way is to model the historic dispersion and deposition on the areas of interest on the basis of historic emission estimates and calculate resulting water and soil concentrations. The end situation of this calculation can then be used as begin situation for the modelling of the present dispersion and deposition. For this approach information on historic emissions must be available.
The second approach is to make an inventory of areas where re-volatilisation occurs and to estimate or measure the source strength of these areas. These area

sources can then be used as input in the atmospheric dispersion model. Note that the source strength (the water and soil concentrations) can be based on measurements or on a combination of measured and modelled concentrations.

4. Critical limits

4.1 Introduction

This chapter deals with deriving effect-based critical limits for aquatic ecosystems. In the AL:ML approach this is the second step of the scheme presented in figure 1.1 in paragraph 1.2. In the PEC:PNEC approach it is the second last step of the scheme. In both approaches, setting critical limits is a step of major importance in the risk assessment. Critical limits should be based on insight in the relation between the chemical status of the water and sediment and the response of one or more biological indicators (an organism or population). In both the AL:ML and PEC:PNEC approaches the ecotoxicologically based 'Predicted No Effect Concentration' (PNEC) is adopted as example for the critical limit but critical limits can also be based on other ecotoxicological threshold values such as the EC50 (the concentration at which 50% of the population shows a (negative) response).
As stated in Chapter 2, the crucial question in choosing the critical limit for risk assessment purposes is: 'What do we want to protect?'. Following the discussions at the Bad Harzburg workshop, it was decided that the risk assessment for POPs should be directed at the following receptors:

1. Lower aquatic organisms such as water flees, and small fish.
2. Higher aquatic organisms such as larger fish and (top-)predators such as fish-eating birds and mammals.
3. Human beings that consume fish.
4. Drinking water based on surface water

In this chapter, methods for deriving critical limits for each of the above mentioned (groups of) receptors are therefore discussed. With respect to the eventual choice of critical limit, this manual has an open structure: One can choose to perform the risk assessment for all receptors and base subsequent actions on the highest PEC:PNEC or AL:ML ratio to be sure of total protection or one can choose to perform the risk assessment for only one specific receptor in order to specifically protect this one. In Annex 1 an overview is given of the critical limits for POPs in water and in related receptors that are operational in various UN-ECE countries.

For (top-)predators the critical limit is often expressed as concentration in their food, for humans the Acceptable Daily Intake (ADI) is often adopted. For (lower) aquatic organisms the concentration in the water is mostly assumed to be the bioavailable concentration. In this chapter the critical limits for all receptors are linked to the concentration in the water by means of models because in this way, the risk assessment model (see Chapter 5) can be used for all types of critical limits without need for changes.

Besides the question of 'What do we want to protect?', one can ask another question, *i.e.* 'What level of protection do we want?'. Here, one can make distinction between protection on the ecosystem level, on the population level and on the individual level. Protection on the individual level is mostly restricted to protection of human health, whereas environmental protection is mostly based on the protection on ecosystem level or population level. Protection of the ecosystem can for example be based on the protection of ecosystem function or structure, on the protection of a certain percentage of species in the ecosystem or on the protection of the most sensitive species or an indicator species in the ecosystem.

In the next paragraph, methods to derive critical limits for each of the above mentioned (groups of) receptors are discussed.

4.2 Methods to derive effect-based critical limits for surface waters

4.2.1 Limits based on direct effects on lower aquatic organisms

In this paragraph two extrapolation methods are presented for deriving critical limits based on direct effects on aquatic organisms. Although there are many other methods to derive critical limits (most of them comparable to the ones presented here), the presented methods are chosen because they are in accordance with recommendations made by the OECD for the aquatic environment (OECD, 1992) and they are widely used. The first method is the most simple one and is based on the so-called modified EPA (Environmental Protection Agency) method (EPA, 1984; Van de Meent *et al.*, 1990; OECD, 1992). It can be used for preliminary effects assessment and has relatively low data requirements. The second method is a more detailed method based on the extrapolation method developed by Aldenberg and Slob (1991, 1993) on the basis of the method of Van Straalen and Denneman (1989). It can be used for more refined effects assessment but data requirements for this method are higher than for the modified EPA method.

Simple method: The modified EPA method

The simple method to derive a critical limit for the aquatic ecosystem, with relatively low data requirements, is based on the modified EPA method. In this method safety factors, the values of which depend on the type and number of available toxicity data, are applied to the toxicity data (Van de Plassche, 1994). In table 4.1 the safety factors of the modified EPA method for aquatic organisms are given.

Table 4.1. Safety factors in the modified EPA method for aquatic organisms.

Type and number of available toxicity data	Safety factor
Lowest acute L(E)C50 or QSAR (Quantitative Structure-Activity Relationship) estimate for acute toxicity	1000
Lowest acute L(E)C50 or QSAR estimate for acute toxicity for minimal algae/crustaceans/fish	100
Lowest chronic NOEC or QSAR estimate for chronic toxicity	10[a]
Lowest chronic NOEC or QSAR estimate for chronic toxicity for minimal algae/crustaceans/fish	10

[a] This value is subsequently compared to the extrapolated value based on acute L(E)C50 toxicity data. The lowest one is selected.

In the modified EPA method both acute and chronic toxicity data are weighted in the following manner (Van de Plassche, 1994):

- If for a single species more than one L(E)C50 or NOEC values are derived for different effect parameters, the lowest is selected.
- If for a single species more than one L(E)C50 or NOEC values are derived for the same effect parameter, a geometric mean value is calculated

The critical limit in the surface water (the Maximum Permissible Concentration in surface water, MPC_{water}) is then equal to the value derived with the modified EPA value:

$$MPC_{water} = \text{EPA-value} \qquad (4.1)$$

where:

MPC_{water} = the critical limit (the Maximum Permissible Concentration) in the surface water ($g.m^{-3}$ water)

EPA-value = the NOEC (No Observed Effect Concentration) for aquatic organisms according to the modified EPA method ($g.m^{-3}$ water)

More detailed method: The statistical extrapolation method

The more complex method to derive critical limits for direct effects on aquatic organisms is based on the statistical extrapolation method of Aldenberg en Slob (1991, 1993). In this method a level of ecosystem protection is chosen in the form of a percentage of species that is protected (*e.g.* 95%) at a given probability (*e.g.* 50% or 95%). The method can be used if at least four NOEC values for different taxonomic groups of terrestrial organisms are available. If for a single species more than one NOEC value for different effect parameters or for the same effect parameter are available, the same weighing procedure is followed as in the modified EPA method. The method is further based on the assumption that the log NOEC values show a logistic distribution (see figure 4.1). In this distribution a percentage of species that one wants to protect is chosen. The associated log NOEC then leaves 100% minus this percentage of species unprotected (p%). This

log NOEC is then called the log Hazardous Concentration for p% of the species (log HC_p). The HC_p can be calculated from the mean and standard deviation of the logistic distribution according to equation 4.2 (generalised from Aldenberg and Slob, 1991):

$$\log HC_p = \mu - \sigma \times 0.55 \times \ln((100-p)/p) \qquad (4.2)$$

where:

HC_p = the Hazardous Concentration that affects p% of the soil species
μ = the mean of the distribution
σ = the standard deviation of the distribution
p = the percentage unprotected species

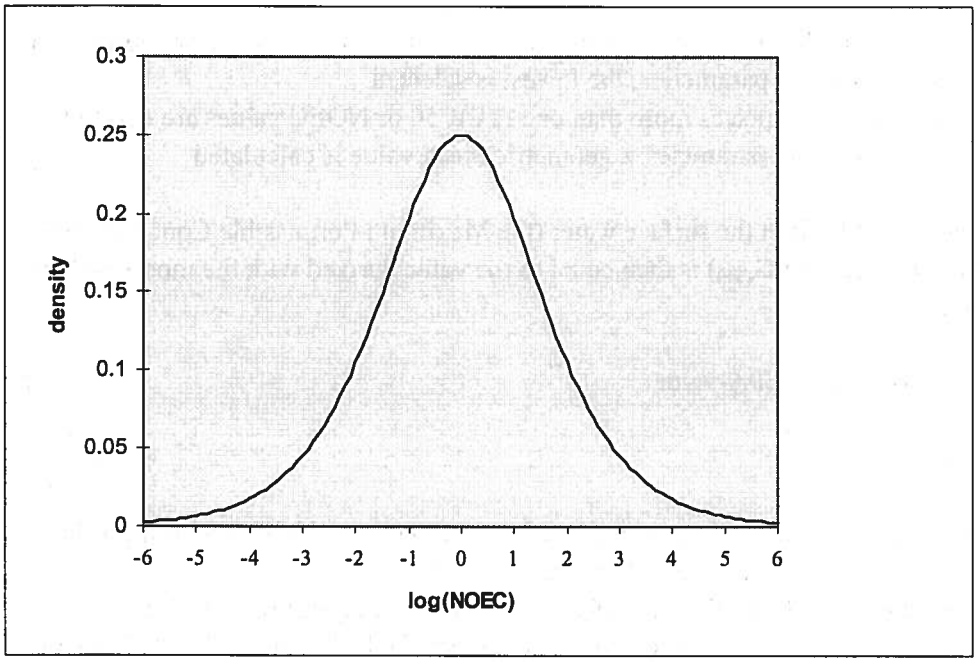

Figure 4.1 *The assumed standard logistic distribution of log(NOEC) values.*

A simple estimate Z for log HC_p neglecting uncertainty due to limited sample size is given in equation 4.3 (generalised from Aldenberg and Slob, 1991):

$$Z = x_m - s_m \times 0.55 \times \ln((100-p)/p) \qquad (4.3)$$

where:

x_m = the sample mean
s_m = the sample standard deviation
m = the number of test organisms

However, this simplification would lead to frequent overprediction (Z is higher than HC_p if m is smaller than infinite). This means that more than p% of the species would be affected. We want however a formula that overestimates log HC_p in a minority of samples only, so that with large *confidence* we can say that no more than p% of the species is affected. Aldenberg and Slob (1991) determined by means of Monte Carlo simulation a table of extrapolation constants for the calculation of the one-sided left confidence limits (50% and 95% confidence) for the logarithmic Hazardous Concentration for 5% of the species on the basis of the logistic distribution. For more details on this extrapolation method, the reader is referred to Aldenberg and Slob (1991).

The critical limit in the surface water (MPC_{water}) can be taken equal to the Hazardous Concentration for p% of the aquatic species, calculated according to Aldenberg and Slob (1991):

$$MPC_{water} = HC_p \qquad (4.4)$$

where:

MPC_{water} = the critical limit (the Maximum Permissible Concentration) in the surface water ($g.m^{-3}$ water)
HC_p = the concentration in the surface water (Hazardous Concentration) that affects p% of the aquatic species ($g.m^{-3}$ water)

4.2.2 Limits based on indirect effects on higher organisms

Several POPs are considered to have a bioaccumulation potential, due to which organisms higher in the food chain may experience secondary poisoning. This means that for some POPs the critical limit based on direct effects on lower organisms may not be sufficient to protect higher organisms too. This depends however on the degree of bioaccumulation and biomagnification on the one hand and the sensitivity of the species at the top of the food chain/food web. In order to be able to derive a critical limit for the aquatic ecosystem based on secondary poisoning one needs a model that links the concentration in the surface water to the effect on organisms at the higher end of the food chain/food web.
Existing models describing the aquatic food web vary in degree of complexity, ranging from relatively simple two step food chains to food webs consisting of four or more trophic levels, including various groups of organisms per trophic level and many interactions between these groups. In this paragraph an example of a relatively simple method, with relatively low data requirements, is presented and some considerations with respect to more complex models are given. The model can be viewed as an example and can be replaced, if preferred, by any other food chain or food web model that connects the critical concentration in the receptor of choice to the concentration in the waterl.

Simple food chain model

As an example of a relatively simple model the two step aquatic food chain model developed by Romijn *et al.* (1993) and refined by Van de Plassche (1994) is presented here. In this model the food chain consists of the path *water -> fish or mussel -> bird/mammal*. For deriving a critical limit in the surface water that takes into account secondary poisoning in this food chain the following algorithms were drawn up:

$$MPC_{water} = (NOEC_{fish\text{-}eater} \times 0.32) / BCF_{fish} \quad (4.5)$$

and

$$MPC_{water} = (NOEC_{mussel\text{-}eater} \times 0.20) / BCF_{mussel} \quad (4.6)$$

where:

MPC_{water} = the critical limit (the Maximum Permissible Concentration) in the surface water ($g.m^{-3}$ water)

$NOEC_{fish\text{-}eater}$ = the critical limit (No Observed Effect Concentration) in the food (*i.e.* fish) of the bird or mammal ($g.kg^{-1}$ fish)

$NOEC_{mussel\text{-}eater}$ = the critical limit (No Observed Effect Concentration) in the food (*i.e.* mussel) of the bird or mammal ($g.kg^{-1}$ mussel)

BCF_{fish} = the ratio (BioConcentration Factor) between the concentrations in fish and water (m^3 water.kg^{-1} fish)

BCF_{mussel} = the ratio (BioConcentration Factor) between the concentrations in mussel and water (m^3 water.kg^{-1} mussel)

The critical limit in the bird or mammal ($NOEC_{fish\text{- or mussel-eater}}$) can be determined with the modified EPA method for birds and mammals. This is again a decision scheme for applying safety factors to toxicity data determined for birds or mammals. The value of the safety factors depend on the type and number of available toxicity data (Van de Plassche, 1994). In table 4.3 the safety factors of the modified EPA method for birds and mammals are given. The factors 0.32 and 0.20 are correction factors to account for the differences in caloric content of laboratory food (mostly cereals) and fish and mussels respectively (Ruys and Pijnenburg, 1991).

Table 4.3. Safety factors in the modified EPA method for birds and mammals.

Type and number of available toxicity data	Safety factor
Less than 3 acute L(E)C50s and no chronic NOECs	1000
At least 3 acute L(E)C50s and no chronic NOECs	100
Less than 3 chronic NOECs	10[a]
3 Chronic NOECs	10

[a] This value is subsequently compared to the extrapolated value based on acute L(E)C50 toxicity data. The lowest one is selected.

The same weighing of data is performed as described under the simple method of paragraph 4.2.1.

If no experimental data are available, the BCF_{fish} or BCF_{mussel} can be derived using a QSAR (Quantitative Structure Activity Relationship). QSARs found in the literature for BCFs (in $l.kg^{-1}$) of organic compounds in fish (MacKay, 1982) and mussels (Everts *et al.*, 1992) are:

$$BCF_{fish} = 0.048 \times K_{ow} \quad (4.7)$$

$$BCF_{mussel} = 0.013 \times K_{ow} \quad (4.8)$$

where:

K_{ow} = the octanol/water partitioning coefficient (-)

More detailed food web model

The relatively simple model presented in the previous section can be made more complex by describing processes in more than detail or by adding 'branches' to the food chain to create a food web. With respect to describing processes in more detail, the description of POP uptake by fish can be mentioned as an example. In the simple model this uptake is described by the bioconcentration factor which assumes that the major pathway of uptake is directly from the water. From several (mostly modelling) studies it appears however that especially at higher K_{ow} values this is not the case. Thomann (1981, 1989) for example, found for organic compounds with log K_{ow} values > 5 that uptake through food chains becomes significant. The same was found by Gobas *et al.* (1988) who derived a relationship between uptake efficiency of organic chemicals from food by fish and the octanol/water partition coefficient. They modelled uptake of the chemical by fish by taking into account uptake from water through the gills and from food, and losses by elimination to the water through the gills, elimination in the faeces and metabolic transformation. They defined rate constants for all of these processes and calculated the resulting concentration in the fish. However, most of these constants are not available for many combinations of fish and organic chemicals, which makes the model difficult to apply for the calculation of effect-based maximum loads of POPs for surface waters.

With respect to adding 'branches' to the simple two-step food chain the same problem arises: Although it is possible to describe a more complex (and probably more realistic) aquatic food web with several trophic levels, it remains difficult to acquire the larger number of parameter values needed in the more complex model.

4.2.3 Limits based on effects on human health

Humans health criteria can also be used to determine critical limits for risk assessment for POPs in aquatic ecosystems. The most probable route from the aquatic system to the uptake by humans is through consumption of fish or through drinking water based on the surface water. In both cases, a critical fish and/or water concentration can be derived from the combination of the Acceptable Daily Intake (ADI) of the POP by a human being and his (assumed) consumption

pattern. This critical fish concentration can be coupled to a critical water concentration with the bioconcentration factor (BCF) mentioned in the previous paragraph.

5. Calculation methods

5.1 Introduction

In this chapter, models are described that can be used for performing risk assessments for POPs in aquatic ecosystems (lakes). This concerns both steps 3 (selecting the method (model)) and 5 (calculating the Predicted Environmental Concentration (PEC) or the effect-based Maximum Load (ML)) in the PEC:PNEC and AL:ML approaches of figure 1.1 in paragraph 1.2. In this manual, step 3 is choosing between a simple model with relatively low data requirements and a more elaborated model with higher data requirements. Step 5 gets its final form for both approaches in paragraph 5.5 with the equations to calculate the PEC or ML. Paragraphs 5.2, 5.3 and 5.4 form the introduction to the final equations in paragraph 5.5.

Most limits presented in the previous chapter were translated to and expressed in aquatic concentrations. This was the case for direct effects on lower aquatic organisms and indirect effects on higher organisms including human beings that use the surface water as (basis for) drinking water or that consume fish from this water. The general approach described in this chapter is therefore based on a critical concentration in the lake water. As many lakes are not isolated hydrological units, the general approach calculates the PEC for the lake itself but the effect-based maximum load (ML) for the catchment that drains into the lake. This is done by first calculating the effect-based maximum load for the lake itself on the basis of the chosen critical limit and of its properties such as its dimensions, its mass flow of water and the properties and behaviour of its suspended particles and sediment. This maximum load is then translated to the maximum (diffuse) load for the catchment area by taking into account the total surface area of the catchment and the mean residence time of the POP in this catchment before it arrives at the lake. The advantage of this two-step approach is that it makes clear that the effect-based maximum load for a lake is a combination of the processes in the lake, determining the actual concentration, and the route(s) of the POP to the lake. A further advantage is that the two-step approach enables the individual use of the intermediate result, *i.e.* the effect-based maximum total load for the lake itself, for other purposes. The models for calculating the PEC and the effect-based maximum load for the lake itself are based on a steady-state mass balance equation, which describes the input and output (loss) fluxes into and out of the lake. Furthermore, the models are based on the concept of equilibrium partitioning between the different phases. This means that the models described in this manual are very much comparable to most commonly used models for modelling the behaviour of organic pollutants in aquatic systems such as presented by Mackay *et al.* (1985) and Van Pagee and Villars (1994).
In separate paragraphs at the end of this chapter an alternative approach, based on a critical limit in the sediment is presented and some considerations with respect to

an empirical approach are given. Finally the possibilities of calculating effect-based maximum loads for seas are discussed.
In Annex 2 a list is presented of the symbols that are used in the equations in the following paragraphs. The input data that are required for the models are described separately in Chapter 6.

5.2 General approach

5.2.1 Major assumptions

The models for calculating the PEC and the effect-based maximum total load for the lake itself are based on the following assumptions:

1. The concentration of the POP in the aquatic system (including the sediment compartment) has reached a steady-state, *i.e.* the concentration does not change in time any more because the amount of POP entering the aquatic system is equal to the amount that leaves the system.
2. The POP present in the system follows the concept of equilibrium partitioning. In the case of the aquatic system this means that it is assumed that the POP in the water compartment partitions over the dissolved phase and the adsorbed phase of suspended particles and that the POP in the sediment compartment partitions over the pore water (dissolved) phase and the adsorbed phase of the sediment. In both cases it is assumed that the concentration in each of these phases is in a state of equilibrium at any moment.
3. Both the water compartment and the sediment compartment are homogeneously mixed. Due to this, system properties and concentrations of the pollutant do not show horizontal or vertical variation within the compartments.
4. Sedimentation at least equals resuspension of sediment particles.

In Chapter 7 on uncertainties, the implications of the diverse assumptions is discussed.

5.2.2 Steady-state mass balance equation

The steady-state mass balance of organic micropollutants in the water compartment of the lake is characterised by a total output flux that is equal to the total input flux. For the risk assessment scheme in this manual, the following general steady-state equation is adopted for the water compartment:

$$X_{tl} + X_{res} = X_{vol} + X_{lo} + X_{deg,w} + X_{sed} + X_{inf} + X_{dif} \qquad (5.1)$$

where:

X_{tl} = the total load of compound X on the lake ($g.m^{-2}.yr^{-1}$)
X_{res} = the amount of compound X that is transported from the sediment compartment to the water compartment by resuspension ($g.m^{-2}.yr^{-1}$)

X_{vol} = the loss of compound X by volatilisation ($g.m^{-2}.yr^{-1}$)
X_{lo} = the loss of compound X by lateral outflow of water ($g.m^{-2}.yr^{-1}$)
$X_{deg,w}$ = the total loss of compound X by degradation in the water compartment ($g.m^{-2}.yr^{-1}$)
X_{sed} = the amount of compound X that is transported from the water compartment to the sediment compartment by sedimentation ($g.m^{-2}.yr^{-1}$)
X_{inf} = the amount of compound X that is transported from the water compartment to the sediment compartment by infiltrating water ($g.m^{-2}.yr^{-1}$)
X_{dif} = the amount of compound X that is transported from the water compartment to the sediment compartment or vice versa by diffusion ($g.m^{-2}.yr^{-1}$)

For the sediment compartment the steady-state mass balance has the following form:

$$X_{sed} + X_{dif} + X_{inf} = X_{res} + X_{deg,sed} + X_{bur} + X_{sp} \quad (5.2)$$

where:

$X_{deg,sed}$ = the total loss of compound X by degradation in the sediment compartment ($g.m^{-2}.yr^{-1}$)
X_{bur} = the loss of compound X as a result of burial of sediment ($g.m^{-2}.yr^{-1}$)
X_{sp} = the loss of compound X by seepage ($g.m^{-2}.yr^{-1}$)

Figure 5.1 gives a schematic representation of the elements of the mass balance for POPs in an aquatic system.

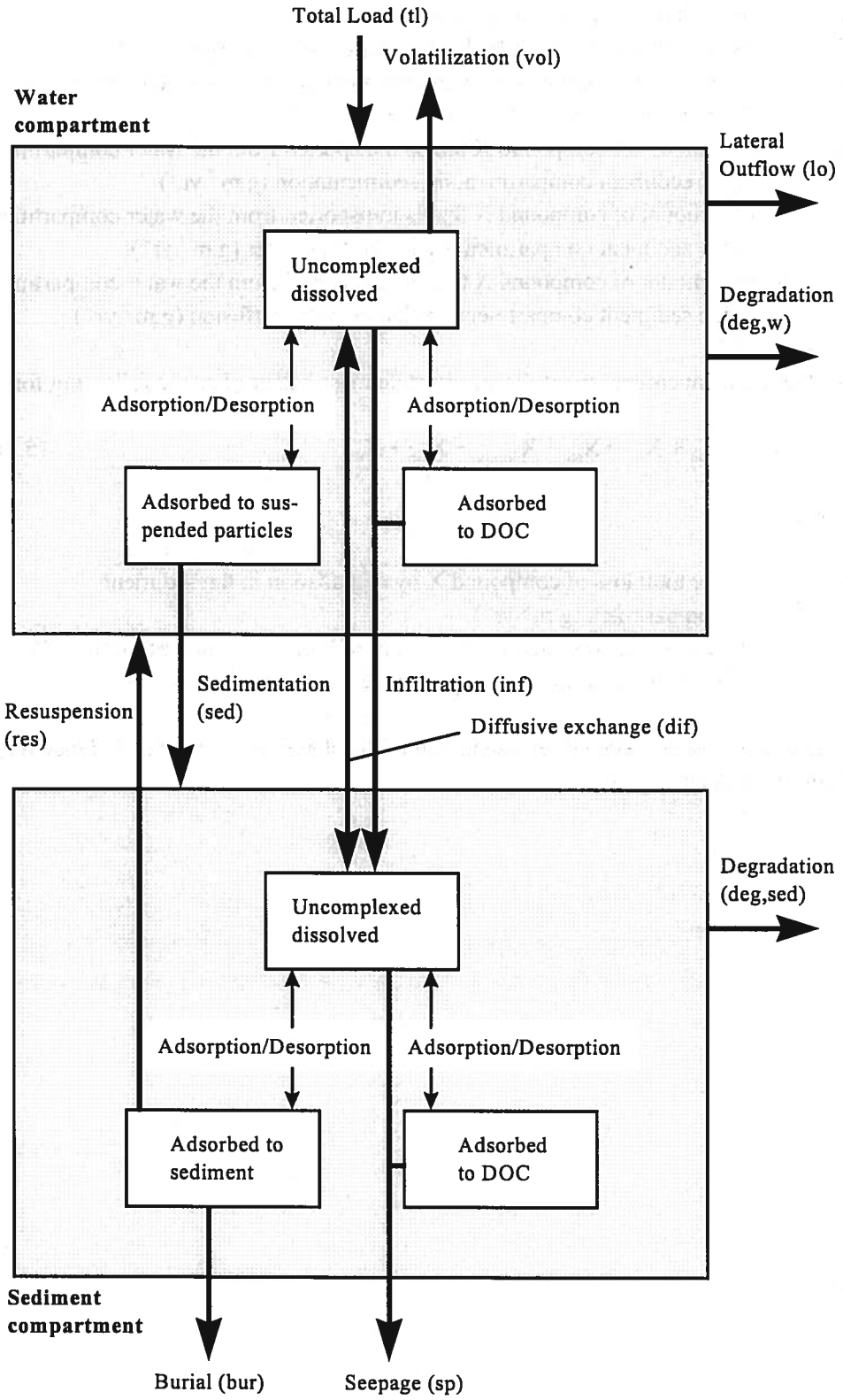

Figure 5.1 *Schematic representation of the elements of the mass balance for POPs in an aquatic system.*

5.3 Calculation of POP fluxes

When determining the fluxes that influence the surface water and sediment quality, three types of fluxes can be distinguished, *i.e.* (externally determined) input fluxes, output fluxes and exchange fluxes between the water compartment and the sediment compartment. In the next three paragraphs these three types of fluxes are described.

5.3.1 Input fluxes

As described in Chapter 3, the actual load on the aquatic ecosystem may result from several processes. The total load of POPs on the lake X_{tl} consists of direct loads and indirect loads. Direct loads are for example atmospheric deposition on its water surface and other direct loads due to emissions from *e.g.* ships, households and industry. Indirect loads are loads that reach the lake via the incoming water and may be the result of atmospheric deposition or other loads on the catchment area, from which it may reach the lake after leaching and/or surface runoff .

$$X_{tl} = X_{dl} + X_{il} \tag{5.3}$$

where:

X_{dl} = the direct load of compound X on the lake ($g.m^{-2}.yr^{-1}$)
X_{il} = the indirect load of compound X on the lake ($g.m^{-2}.yr^{-1}$)

and:

$$X_{dl} = X_{dd} + X_{dol} \tag{5.3a}$$

where:

X_{dd} = the direct atmospheric deposition flux of compound X on the lake ($g.m^{-2}.yr^{-1}$)
X_{dol} = the direct other loads of compound X on the lake ($g.m^{-2}.yr^{-1}$)

and:

$$X_{il} = X_{id} + X_{iol} \tag{5.3b}$$

where:

X_{id} = the indirect load of compound X on the lake, coming from atmospheric deposition flux on the catchment ($g.m^{-2}.yr^{-1}$)
X_{iol} = the indirect load of compound X on the lake, coming from other loads on the catchment ($g.m^{-2}.yr^{-1}$)

Direct atmospheric deposition

Atmospheric deposition direct onto the lake may be divided into dry deposition and wet deposition. A further distinction can be made between deposition of aerosol-bound compounds and gaseous compounds. For a synopsis on the calculation of atmospheric deposition of POPs, the reader is referred to Chapter 3.

Direct other loads

Other loads of POP on the lake may be due to of emissions from ships, households or industries. As determining direct other loads is rather site-specific and rather straightforward, calculating other loads is not elaborated here. This does however not mean that direct other loads can not be very important and in many situations can even be the dominant source of contamination.

Indirect loads (both atmospheric deposition and other loads)

Lakes are also contaminated by lateral inflow of water carrying pollutants. This water and pollutants may come from sources such as surface runoff and leaching of atmospheric deposited POPs from soils in the entire catchment area and from other (for example agricultural) sources in the catchment area.. In order to be able to calculate a PEC in the lake as a result of loads on the catchment and to be able to translate an effect-based maximum load for the lake itself to an effect-based maximum load for the catchment, we need to relate loads on the lake to loads on the catchment area. For substances that do not degrade this is possible under the assumption that the load on the catchment area is a diffuse load. Under steady-state conditions, the same amount of a non-degrading pollutant that enters a catchment area, passes the outlet point of the catchment area. The lake for which the PEC and effect-based maximum load is calculated, is assumed to form this outlet. The relation between the indirect load on the lake and the mean (diffuse) load on the catchment area can then be calculated according to equation 5.4a:

$$X_{il} = \frac{X_{cl} \times A_c}{A_l} \qquad (5.4a)$$

where:

X_{cl} = the mean (diffuse) load of compound X on the catchment area ($g.m^{-2}.yr^{-1}$)
X_{il} = the indirect load of compound X on the lake that comes from the catchment ($g.m^{-2}.yr^{-1}$)
A_c = the surface area of the catchment area (m^2)
A_l = the surface area of the lake (m^2)

In the case of a degradable compound it is less simple to relate the load on the catchment area to the indirect load on the lake because one must have information on the mean residence time of the compound in the catchment area (the mean time needed to travel from the point of entry in the catchment area to the lake). If this

information is available, an estimation can be made of the fraction of the compound that is degraded during its travel from the catchment to the lake. Assuming first order degradation during this transport, the relation between load on the catchment X_{cl} and indirect load on the lake X_{il} can be described according to equation 5.4b:

$$X_{il} = \frac{X_{cl} \times A_c \times e^{-kdeg \times t}}{A_l} \qquad (5.4b)$$

where:

t = the mean residence time in the catchment area between entry in the catchment area and arrival at the lake (yr)
kdeg = the overall rate constant for degradation of compound X in the catchment (yr^{-1})

5.3.2 Output fluxes

The total loss of POPs from the aquatic system (including the sediment) results from volatilisation from the water compartment, degradation in both the water and sediment compartment, lateral outflow from the water compartment, burial of sediment and seepage of water from the considered sediment layer to deeper sediment layers.

Volatilisation

Volatilisation of gaseous compounds from the water to the air can be regarded as inverse dry deposition. Therefore, (re-)volatilisation should theoretically already be taken into account during the calculation of the atmospheric deposition flux on surface water. Up to now only a few model studies have been carried out in which the bi-directional flux of substances has been taken into account, *i.e.* consider *net*-deposition as the sum of dry deposition and re-volatilisation instead of dry deposition alone (Van Pul *et al.*, 1996). In a number of studies, the exchange process of a substance on a yearly basis is parameterised with a so-called *effective* deposition velocity (Van Jaarsveld *et al.*, 1997). Models in which this process is modelled dynamically are under development and will become available for operational use in the near future (Galperin and Maslyaev, 1996; Jacobs and Van Pul, 1996). However, if the re-volatilisation is not incorporated in the atmospheric transport model, volatilisation must be treated separately. Below, this volatilisation is parameterised.

Volatilisation of a gaseous organic compound from a surface water to the air can be calculated according to the classic double film theory described by Liss and Slater (1974):

$$X_{vol} = k_l \times (([X]_{unc,w} - [X]_{atm}/K_h) \qquad (5.5a)$$

where:

$[X]_{unc,w}$ = the uncomplexed dissolved concentration of compound X in the surface water ($g.m^{-3}$)
$[X]_{atm}$ = the concentration of compound X in the atmosphere ($g.m^{-3}$)
K_h = Henry's law constant (-)
k_l = the transfer coefficient between water and air ($m.yr^{-1}$)

Of course volatilisation only occurs if $[X]_{unc,w}$ is larger than $[X]_{atm}/K_h$. As most atmospheric models do not take into account the concentration already present in the water in the calculation of atmospheric deposition, the calculation of volatilisation should not take into account the atmospheric concentration to avoid inconsistencies. Therefore X_{atm} is assumed to be zero and equation 5.5a changes into:

$$X_{vol} = k_l \times [X]_{unc,w} \qquad (5.5b)$$

The calculation of transfer coefficient k_l can be described according to Liss and Slater (1974):

$$1/k_l = 1/(k_{atm} \times K_h) + 1/k_w \qquad (5.6)$$

where:

k_{atm} = the mass transfer coefficient in the air at the air-water interface ($m.yr^{-1}$)
k_w = the mass transfer coefficient in the water at the air-water interface ($m.yr^{-1}$)

Lateral outflow

In non-isolated lakes, the water that laterally flows in must also flow out of the system again (neglecting evaporation). With the outflowing water the pollutant also leaves the system. This lateral output X_{lo} can be calculated according to:

$$X_{lo} = [X]_{tot,w} \times Q_l / A_l \qquad (5.7)$$

where:

$[X]_{tot,w}$ = the total concentration of compound X in the water ($g.m^{-3}$)
Q_l = the mass flow of water through the lake ($m^3.yr^{-1}$)

Degradation

Both in the water compartment and the sediment compartment of the lake, degradation of organic compounds may play a role. In the water compartment degradation can be the result of photolysis in the surface layer, hydrolysis or

biodegradation. In the sediment compartment hydrolysis and biodegradation are the main processes. For the water compartment equation 5.8 is adopted:

$$X_{deg,w} = X_{ph,w} + X_{hy,w} + X_{bd,w} \quad (5.8)$$

where:

$X_{ph,w}$ = the loss of compound X from the water compartment by photolysis ($g.m^{-2}.yr^{-1}$)
$X_{hy,w}$ = the loss of compound X from the water compartment by hydrolysis ($g.m^{-2}.yr^{-1}$)
$X_{bd,w}$ = the loss of compound X from the water compartment by biodegradation ($g.m^{-2}.yr^{-1}$)

For the sediment compartment equation 5.9 is adopted:

$$X_{deg,sed} = X_{hy,sed} + X_{bd,sed} \quad (5.9)$$

where:

$X_{hy,sed}$ = the loss of compound X from the sediment compartment by hydrolysis ($g.m^{-2}.yr^{-1}$)
$X_{bd,sed}$ = the loss of compound X from the sediment compartment by biodegradation ($g.m^{-2}.yr^{-1}$)

Since in most laboratory and field experiments no differentiation can be made between the relative importance of the different processes, observed degradation rates are mostly overall degradation rates. In the approach presented here this overall degradation is described by a first order reaction according to:

$$X_{deg,w} = k_{deg,w} \times [X]_{tot,w} \times z_w \quad (5.10)$$

$$X_{deg,sed} = k_{deg,sed} \times [X]_{tot,sed} \times z_{sed} \quad (5.11)$$

where:

$[X]_{tot,sed}$ = the total concentration of compound X in the sediment ($g.m^{-3}$)
$k_{deg,w}$ = the overall rate constant for degradation in the water (yr^{-1})
$k_{deg,sed}$ = the overall rate constant for degradation in the sediment (yr^{-1})
z_w = the depth of the water compartment (m)
z_{sed} = the depth of the sediment compartment (m)

Burial of sediment

When the sedimentation flux of suspended particles from the water compartment to the sediment compartment is larger than the resuspension flux of sediment

particles to the water compartment, the sediment layer will grow. As it is common in aquatic models to consider only the sediment's top layer of a fixed thickness, loss of pollutant from the considered system will occur by burial of the sediment. This process is described by equation 5.12:

$$X_{bur} = ctX_{sed} \times (F_{sed}-F_{res}) \times \rho_{sed} \qquad (5.12)$$

where:

ctX_{sed} = the adsorbed content of compound X in the sediment ($g.kg^{-1}$)
F_{sed} = the sedimentation flux of suspended particles ($m.yr^{-1}$)
F_{res} = the resuspension flux of sediment particles ($m.yr^{-1}$)
ρ_{sed} = the dry bulk density of the sediment ($kg.m^{-3}$)

Seepage

When water from the water compartment infiltrates into the sediment layer and seeps into deeper layers, the pollutant dissolved in the pore water is lost from the considered aquatic system. This loss process is described by equation 5.13:

$$X_{sp} = [X]_{tot,pw} \times F_{sp} \qquad (5.13)$$

where:

$[X]_{tot,pw}$ = the total concentration of compound X in the pore water ($g.m^{-3}$)
F_{sp} = the flux of water seeping through the sediment ($m.yr^{-1}$)

5.3.3 Exchange fluxes between water and sediment

Infiltration

When water from the water compartment infiltrates into the sediment layer, the pollutant dissolved in the water is transported from the water compartment to the sediment compartment. This exchange process is described by equation 5.14:

$$X_{inf} = ([X]_{unc,w} + ctX_{doc,w} \times DOC_w) \times F_{sp} \qquad (5.14)$$

where:

$ctX_{doc,w}$ = the content of compound X on (complexed with) dissolved organic carbon in the surface water ($g.kg^{-1}$)
DOC_w = the concentration of dissolved organic carbon in the water ($kg.m^{-3}$)

Sedimentation

Sedimentation is the result of the settling of suspended particles. As a result of this process, the pollutant adsorbed to the suspended particles is transported from the

water compartment to the sediment compartment. This exchange process is described by equation 5.15:

$$X_{sed} = ctX_{sus} \times F_{sed} \times \rho_{sed} \quad (5.15)$$

where:

ctX_{sus} = the adsorbed content of compound X in suspended particles ($g.kg^{-1}$)

Resuspension

Resuspension of sediment particles is the result of turbulence at the water-sediment interface. As a result of this process, the pollutant adsorbed to the sediment particles is transported from the sediment compartment to the water compartment. This exchange process is described by equation 5.16:

$$X_{res} = ctX_{sed} \times F_{res} \times \rho_{sed} \quad (5.16)$$

Diffusive exchange

When the dissolved (uncomplexed) concentration of the pollutant in the water is not equal to its concentration in the pore water of the sediment, there will be a diffusive transport from the compartment with the higher concentration to the compartment with the lower concentration. This process is described by equation 5.17.

$$X_{dif} = D_{eff} \times ([X]_{unc,w} - [X]_{unc,pw}) / z_{dif} \quad (5.17)$$

where:

$[X]_{unc,pw}$ = the uncomplexed dissolved concentration of compound X in the pore water of the sediment ($g.m^{-3}$)
D_{eff} = the effective diffusivity in the sediment ($m^2.yr^{-1}$)
z_{dif} = the diffusion path length in the sediment at the water-sediment interface (m)

The diffusivity in the sediment layer can be calculated according to Mackay *et al.* (1985):

$$D_{eff} = D_{mol,w} \times (p)^{1.5} \quad (5.18)$$

where:

$D_{mol,w}$ = the molecular diffusivity in the water phase ($m^2.yr^{-1}$)
p = the porosity (volumetric water content) of the sediment ($m^3.m^{-3}$)

or according to any other equation which takes into account the sediment porosity available for diffusion and the path lengthening for diffusion due to the fact that the individual pores do not form straight channels.

5.4 Equilibrium partitioning in aquatic systems

As remarked earlier, the models in this manual are based on the concept of equilibrium partitioning between water and suspended particles and between pore water and sediment. According to this concept it is assumed that an organic compound in the water and sediment will partition over two phases according to equations 5.19 to 5.22 instantaneously at any time:

$$ctX_{sus} = K_{p,sus} \times [X]_{unc,w} \quad (5.19)$$

$$ctX_{sed} = K_{p,sed} \times [X]_{unc,pw} \quad (5.20)$$

$$ctX_{doc,w} = K_{p,doc} \times [X]_{unc,w} \quad (5.21)$$

$$ctX_{doc,pw} = K_{p,doc} \times [X]_{unc,pw} \quad (5.22)$$

ctX_{sus} = the adsorbed content of compound X in suspended particles ($g.kg^{-1}$)
ctX_{sed} = the adsorbed content of compound X in the sediment ($g.kg^{-1}$)
$ctX_{doc,w}$ = the content of compound X on (complexed with) dissolved organic carbon in the surface water ($g.kg^{-1}$)
$ctX_{doc,pw}$ = the content of compound X on (complexed with) dissolved organic carbon in the pore water of the sediment ($g.kg^{-1}$)
$[X]_{unc,w}$ = the uncomplexed dissolved concentration of compound X in the water ($g.m^{-3}$)
$[X]_{unc,pw}$ = the uncomplexed dissolved concentration of compound X in the pore water of the sediment ($g.m^{-3}$)
$K_{p,sus}$ = the adsorption coefficient of compound X to suspended particles ($m^3.kg^{-1}$)
$K_{p,sed}$ = the adsorption coefficient of compound X to sediment ($m^3.kg^{-1}$)
$K_{p,doc}$ = the adsorption coefficient of compound X to dissolved organic carbon ($m^3.kg^{-1}$)

Further the total concentrations in water, pore water and sediment are described by equations 5.23 to 5.25 respectively:

$$[X]_{tot,w} = [X]_{unc,w} + ctX_{doc,w} \times DOC_w + ctX_{sus} \times sus \quad (5.23)$$

$$[X]_{tot,pw} = [X]_{unc,pw} + ctX_{doc,pw} \times DOC_{pw} \quad (5.24)$$

$$[X]_{tot,sed} = ([X]_{unc,pw} + ctX_{doc,pw} \times DOC_{pw}) \times p + ctX_{sed} \times \rho_{sed} \quad (4.25)$$

where:

p	=	the porosity (volumetric water content) of the sediment ($m^3.m^{-3}$)
sus	=	the concentration of suspended particles in the water ($kg.m^{-3}$)
$[X]_{tot,w}$	=	the total concentration of compound X in the water ($g.m^{-3}$)
$[X]_{tot,pw}$	=	the total concentration of compound X in the pore water ($g.m^{-3}$)
$[X]_{tot,sed}$	=	the total concentration of compound X in the sediment ($g.m^{-3}$)
DOC_w	=	the concentration of dissolved organic carbon in the water ($kg.m^{-3}$)
DOC_{pw}	=	the concentration of dissolved organic carbon in the pore water ($kg.m^{-3}$)

In order to describe ratio's between the total concentration and the contributing concentrations more directly, the following relationships can be used:

$$[X]_{tot,w} = [X]_{unc,w} \times R_{unc,w} \quad (5.26)$$

$$[X]_{tot,w} = ctX_{doc,w} \times R_{doc,w} \quad (5.27)$$

$$[X]_{tot,w} = ctX_{sus} \times R_{sus} \quad (5.28)$$

$$[X]_{tot,sed} = [X]_{unc,pw} \times R_{unc,pw} \quad (5.29)$$

$$[X]_{tot,sed} = ctX_{doc,pw} \times R_{doc,pw} \quad (5.30)$$

$$[X]_{tot,sed} = ctX_{sed} \times R_{sed} \quad (5.31)$$

where:

$$R_{unc,w} = (1 + sus \times K_{p,sus} + DOC_w \times K_{p,doc}) \quad (5.32)$$

$$R_{doc,w} = R_{unc,w} / K_{p,doc} \quad (5.33)$$

$$R_{sus} = R_{unc,w} / K_{p,sus} \quad (5.34)$$

$$R_{unc,pw} = (p + \rho_{sed} \times K_{p,sed} + p \times DOC_{pw} \times K_{p,doc}) \quad (5.35)$$

$$R_{doc,pw} = R_{unc,pw} / K_{p,doc} \quad (5.36)$$

$$R_{sed} = R_{unc,pw} / K_{p,sed} \quad (5.37)$$

and:

$R_{unc,w}$ = the ratio between total concentration and uncomplexed dissolved concentration in the water (-)
$R_{doc,w}$ = the ratio between total concentration in the water and adsorbed concentration on dissolved organic carbon (DOC) ($kg.m^{-3}$)
R_{sus} = the ratio between total concentration in the water and adsorbed concentration on suspended particles ($kg.m^{-3}$)
$R_{unc,pw}$ = the ratio between total concentration in the sediment and uncomplexed dissolved concentration in the pore water of the sediment (-)
$R_{doc,pw}$ = the ratio between total concentration in the sediment and adsorbed concentration on dissolved organic carbon (DOC) in the pore water of the sediment ($kg.m^{-3}$)
R_{sed} = the ratio between total concentration in the sediment and adsorbed concentration in the sediment ($kg.m^{-3}$)

Adsorption of organic compounds in suspended particles and in the sediment is again assumed to be linearly related to the organic carbon content of the suspended particles and the sediment:

$$K_{p,sus} = K_{oc} \times fr_{oc,sus} \quad (5.38)$$

$$K_{p,sed} = K_{oc} \times fr_{oc,sed} \quad (5.39)$$

where:

K_{oc} = the adsorption coefficient to organic carbon ($m^3.kg^{-1}$)
$fr_{oc,sus}$ = the fraction organic carbon in suspended particles ($kg.kg^{-1}$)
$fr_{oc,sed}$ = the fraction organic carbon in the sediment ($kg.kg^{-1}$)

Adsorption of organic compounds to dissolved organic carbon is directly coupled to the K_{oc} according to equation 5.40:

$$K_{p,doc} = K_{oc} \times x_{doc} \quad (5.40)$$

where:

x_{doc} = a factor to account for the less efficient adsorption to DOC with respect to particulate organic carbon (-)

5.5 Calculation of the Predicted Environmental Concentration (PEC) or the effect-based Maximum Load (ML)

In this paragraph simple and more elaborated models, based on the steady-state mass balance equation and equilibrium partitioning as described in the previous paragraphs, are described for use in risk assessments of POPs in aquatic

ecosystems. As explained earlier the models are comparable to other commonly used models to describe the behaviour of organic pollutants in aquatic systems (Mackay *et al.*, 1985; Van Pagee and Villars, 1994. In paragraph 5.5.1 models to calculate the PEC for the PEC:PNEC approach of figure 1.1 (steps 3 and 5) in paragraph 1.2 are presented. In paragraph 5.5.2 models to calculate the effect-based Maximum Load (ML) for the AL:ML approach of figure 1.1 (steps 3 and 5) in paragraph 1.2 are presented. In both paragraphs, step 3 is choosing between a simple model with relatively low data requirements and a more elaborated model with higher data requirements. Step 5 implies the application of the chosen model to the ecosystem of concern.

5.5.1 Predicted Environmental Concentration

Simple PEC model

Calculating a PEC with the complete mass balance equations 5.1 or 5.2 implies that a relatively large number of input parameters is needed with these equations. As values for these parameters are not always readily available, it is often desirable to start with a more simplified form of the mass balance equations and associated calculation methods. Therefore a relatively simple model for the calculation of the PEC in the water is presented below, in which the processes of volatilisation, infiltration into the sediment, resuspension of sediment and diffusive exchange between the water column and the sediment are not taken into account and the only processes included are lateral outflow, degradation in water and net sedimentation. This means that the mass balance equation 5.1 for POPs in the water column reduces to:

$$X_{tl} = X_{lo} + X_{deg,w} + X_{netsed} \qquad (5.41)$$

where:

$$X_{netsed} = ctX_{sus} \times F_{netsed} \times \rho_{sed} \qquad (5.42)$$

and where:

F_{netsed} = the net sedimentation flux of suspended particles ($m.yr^{-1}$)

Using equation 5.26 to 5.28 to express all processes mentioned in equation 5.41 in terms of total concentration in the water $[X]_{tot,w}$, the expression to calculate the steady-state concentration in the water compartment (the Predicted Environmental Concentration) becomes:

$$[X]_{tot,w} = \frac{X_{tl}}{Q_l/A_l + (k_{deg,w} \times z_w) + (F_{netsed} \times \rho_{sed}/R_{sus})} \qquad (5.43)$$

where:

$[X]_{tot,w}$ = the Predicted Environmental Concentration in water (PEC; $g.m^{-3}$)

If the mass balance equation for the sediment 5.2 is simplified to include only degradation in the sediment, burial and net sedimentation, it reduces to:

$$X_{netsed} = X_{deg,sed} + X_{bur} \qquad (5.44)$$

where:

$$X_{bur} = ctX_{sed} \times F_{netsed} \times \rho_{sed} \qquad (5.45)$$

Using equation 5.29 to 5.31 to express the processes mentioned in equation 5.44 in the total concentration in the sediment $[X]_{tot,sed}$, the expression to calculate the steady-state concentration in the sediment compartment (the Predicted Environmental Concentration) becomes:

$$[X]_{tot,sed} = \frac{[X]_{tot,w} \times R_{unc,pw} \times (F_{netsed} \times \rho_{sed} \times K_{p,sus})}{R_{unc,w} \times ((k_{deg,sed} \times z_{sed} \times R_{unc,pw}) + (F_{netsed} \times \rho_{sed} \times K_{p,sed}))} \qquad (5.46)$$

$[X]_{tot,sed}$ = the Predicted Environmental Concentration in sediment (PEC; $g.kg^{-1}$)

The contribution of atmospheric deposition and other diffuse loads in the catchment area to the total load and therewith to the PEC in the lake, can be calculated with equations 5.4a and 5.4b.

Elaborated PEC model

When all processes of mass balance equation 5.1 are taken into account and are expressed in terms of total concentration in the water $[X]_{tot,w}$ and total concentration in the sediment $[X]_{tot,sed}$, the expression to calculate the steady-state concentration in the water compartment (the Predicted Environmental Concentration) becomes:

$$X_{tl} = \qquad (5.47)$$

$$(k_l \times [X]_{tot,w} / R_{unc,w}) + ([X]_{tot,w} \times Q_l/A_l) + (k_{deg,w} \times [X]_{tot,w} \times z_w) +$$

$$(((([X]_{tot,w} / R_{unc,w}) + ([X]_{tot,w} / R_{doc,w}) \times DOC_w) \times F_{sp}) + ((([X]_{tot,w} / R_{sus}) \times F_{sed} \times \rho_{sed}) +$$

$$(D_{eff} \times ((([X]_{tot,w} / R_{unc,w}) - ([X]_{tot,sed} / R_{unc,pw})) / z_{dif}) - ((([X]_{tot,sed} / R_{sed}) \times F_{res} \times \rho_{sed})$$

The relationship between the total concentration in the sediment $[X]_{tot,sed}$ and the total concentration in the water $[X]_{tot,w}$ can be derived from the steady-state mass balance equation for the sediment 5.2 and the appropriate equations presented in paragraph 5.3 and can be written as:

$$[X]_{tot,sed} = [X]_{tot,w} \times R_{tot,w} \qquad (5.48)$$

where:

$R_{tot,w}$ = the ratio between the total concentration in the sediment and the total concentration in the water (m^3 water.m^{-3} sediment)

and where:

$$R_{tot,w} = \frac{\left\{\frac{D_{eff}}{z_{dif} \times R_{unc,w}} + \frac{F_{sed} \times \rho_{sed}}{R_{sus}} + \frac{F_{sp}}{R_{unc,w}} + \frac{F_{sp} \times DOC_w}{R_{doc,w}}\right\}}{\left\{\frac{D_{eff}}{z_{dif} \times R_{unc,pw}} + k_{deg,sed} \times z_{sed} + \frac{F_{sed} \times \rho_{sed}}{R_{sed}} + \frac{F_{sp}}{R_{unc,pw}} + \frac{F_{sp} \times DOC_{pw}}{R_{doc,pw}}\right\}} \qquad (5.49)$$

By replacing the distribution ratio's $R_{doc,w}$, $R_{doc,pw}$, R_{sus} and R_{sed} by $R_{unc,w}$ and $R_{unc,pw}$ according to equations 5.32 to 5.37, one can rewrite equation 5.49 as follows:

$$R_{tot,w} = \frac{R_{unc,pw} \times \{(D_{eff}/z_{dif}) + (F_{sed} \times \rho_{sed} \times K_{p,sus}) + (F_{sp} \times (1 + DOC_w \times K_{p,doc}))\}}{R_{unc,w} \times \{(D_{eff}/z_{dif}) + (k_{deg,sed} \times z_{sed} \times R_{unc,pw}) + (F_{sed} \times \rho_{sed} \times K_{p,sed}) + (F_{sp} \times (1 + DOC_{pw} \times K_{p,doc}))\}} \qquad (5.50)$$

Combination of equations 5.47, 5.48 and 5.49 yields an expression with which the total steady-state concentration of compound X in the water (the Predicted Environmental Concentration) can be derived directly from the total load of compound X on the lake:

$$[X]_{tot,w} = X_{tl} / R_{in} \qquad (5.51)$$

where:

R_{in} = the ratio between the total load of compound X on the lake and the total concentration of compound X in the water compartment ($m.yr^{-1}$).

and where:

$$R_{in} = \qquad (5.52)$$

$$(k_l/R_{unc,w}) + (Q_l/A_l) + (k_{deg,w} \times z_w) + (F_{sp} \times (1/R_{unc,w} + DOC_w/R_{doc,w})) +$$

$$((F_{sed} \times \rho_{sed})/R_{sus})) + ((D_{eff}/z_{dif}) \times (1/R_{unc,w} - R_{tot,w}/R_{unc,pw})) - ((F_{res} \times \rho_{sed} \times R_{tot,w})/R_{sed})$$

Combining equation 5.51 with equations 5.26 to 5.31 and 5.48 one can relate the steady-state concentration (PEC) in the other compartments to the total load on the system according to equations 5.53 to 5.58:

$$[X]_{unc,w} = X_{tl} / (R_{in} \times R_{unc,w}) \qquad (5.53)$$

$$ctX_{doc,w} = X_{tl} / (R_{in} \times R_{doc,w}) \qquad (5.54)$$

$$ctX_{sus} = X_{tl} / (R_{in} \times R_{sus}) \qquad (5.55)$$

$$[X]_{unc,pw} = (X_{tl} \times R_{tot,w}) / (R_{in} \times R_{unc,pw}) \qquad (5.56)$$

$$ctX_{doc,pw} = (X_{tl} \times R_{tot,w}) / (R_{in} \times R_{doc,pw}) \qquad (5.57)$$

$$ctX_{sed} = (X_{tl} \times R_{tot,w}) / (R_{in} \times R_{sed}) \qquad (5.58)$$

The contribution of atmospheric deposition and other diffuse loads in the catchment area to the total load and therewith to the PEC in the lake, can be calculated with equations 5.4a and 5.4b.

5.5.2 Effect-based Maximum Load

Simple ML model

Just as in the case of the simple model to calculate the Predicted Environmental Concentration (PEC), the simple model for the calculation of the effect-based Maximum Load (ML) is based on the simplified mass balance equation 5.41. When the total concentration in the water $[X]_{tot,w}$ in equation 5.43 is replaced by one of the critical limits presented in Chapter 4 ($MPC_{water} = [X]_{crit,tot,w}$), the effect-based maximum load on the lake itself ($X_{ml,l}$), based on a critical total concentration in the water, can be calculated according to:

$$X_{ml,l} = [X]_{crit,tot,w} \times (Q_l/A_l + (k_{deg,w} \times z_w) + (F_{netsed} \times \rho_{sed}/R_{sus})) \qquad (5.59)$$

where:

$X_{ml,l}$ = the effect-based maximum load (ML) of compound X for the lake ($g.m^{-2}.yr^{-1}$)

$[X]_{crit,tot,w}$ = the critical total concentration of compound X in the water compartment ($g.m^{-3}$)

If the critical limit in the water compartment is not expressed as a total concentration but as a uncomplexed dissolved concentration, equation 5.59 changes into:

$$X_{ml,l} = [X]_{crit,unc,w} \times (Q_l/A_l + (k_{deg,w} \times z_w) + (F_{netsed} \times \rho_{sed}/R_{sus})) \times R_{unc,w} \qquad (5.60)$$

where:

$[X]_{crit,unc,w}$ = the critical uncomplexed dissolved concentration of compound X in the water compartment ($g.m^{-3}$)

If a critical limit is chosen in the sediment compartment, one derive the equation to calculate the effect-based maximum load for the lake by replacing the total concentration in the sediment $X_{tot,sed}$ in equation 5.46 by a critical adsorbed content in the sediment $ctX_{crit,sed}$ and by relating $[X]_{tot,w}$ to the total load on the lake according to equation 5.61:

$$X_{ml,l} = \frac{ctX_{crit,sed} \times (Q_l/A_l + (k_{deg,w} \times z_w) + (F_{netsed} \times \rho_{sed}/R_{sus})) \times R_{sed}}{(R_{unc,pw} \times (F_{netsed} \times \rho_{sed} \times K_{p,sus})) / (R_{unc,w} \times (k_{deg,sed} \times z_{sed} \times R_{unc,pw}) + (F_{netsed} \times \rho_{sed} \times K_{p,sed}))} \qquad (5.61)$$

where:

$ctX_{crit,sed}$ = the critical adsorbed content of compound X in the sediment compartment ($g.kg^{-1}$)

In order to translate the effect-based maximum load for the lake itself to an effect-based maximum load for the catchment as a whole, the direct loads on the lake X_{dl} (see equation 5.3) must be subtracted from the maximum load for the lake before the load on the catchment can be coupled to the indirect load on the X_{il} according equation to 5.4a or 5.4b. The effect-based maximum load on the catchment based on a critical total concentration in the water of the lake then becomes:

$$X_{ml,c} = \frac{(X_{ml,l} - X_{dl}) \times A_l}{A_c \times e^{-kdeg \times t}} \qquad (5.62)$$

where:

$X_{ml,c}$ = the effect-based maximum load (ML) of compound X for the catchment ($g.m^{-2}.yr^{-1}$)

In equation 5.62 it is assumed that direct atmospheric deposition on the lake is part of the atmospheric deposition on the entire catchment and thus is subject to the degradation during the mean residence time in the catchment. Only when direct atmospheric input on the lake forms the major part of the input on the catchment area (if the lake area forms a substantial part of the catchment area), this assumption leads to an overestimation of the maximum load on the catchment.

Elaborated ML model

Just as in the case of the elaborated PEC model, in the elaborated ML model all processes of mass balance equations 5.1 and 5.2 are taken into account. When the total concentration in the water $[X]_{tot,w}$ in equation 5.51 is replaced by one of the critical limits presented in Chapter 4 (MPC_{water}), the effect-based maximum load on the lake itself ($X_{ml,l}$), based on a critical total ($[X]_{crit,tot,w}$) or uncomplexed dissolved concentration ($[X]_{crit,unc,w}$) in the water, can be calculated according to equations 5.63 and 5.64 respectively:

$$X_{ml,l} = [X]_{crit,tot,w} \times R_{in} \qquad (5.63)$$

or:

$$X_{ml,l} = [X]_{crit,unc,w} \times R_{in} \times R_{unc,w} \qquad (5.64)$$

When a critical limit is chosen in the sediment, the effect-based maximum load can be calculated according to equation 5.65:

$$X_{ml,l} = ctX_{crit,sed} \times R_{in} \times R_{sed} / R_{tot,w} \qquad (5.65)$$

For the explanation of the parameters R_{in}, R_{sed}, $R_{unc,w}$ and $R_{tot,w}$ the reader is referred to equations 5.52, 5.37, 5.32 and 5.50 respectively.

The translation of the effect-based maximum load for the lake itself to an effect-based maximum load for the catchment as a whole is equal to the translation presented with the simple ML model (equation 5.62).

5.6 Alternative approaches

Empirical approaches

Already in the seventies much research has been done within the framework of lake eutrophication in order to define simple empirical relationships between critical phosphorus loads and system properties (Vollenweider, 1975; 1976). The basis for these calculations are simple mass balance models, comparable to the ones described in this manual, and empirical data (measurements). Vollenweider (1975) derived quantitative relations between critical phosphorus loads and the hydraulic load, which equals the ratio between mean water depth and water residence time. In a similar way, Vollenweider (1976) derived empirical relationships between critical phosphorus loads and the relative residence time of

phosphorus (*i.e.* the ratio between phosphorus residence time and water residence time). In this way the calculation of a critical load for phosphorus on a lake was simplified to a very high level.
The above mentioned methods, based on Vollenweider's approach for phosphorous has large advantages. When data are available on total concentrations of a certain POP in lake water and incoming water, an empirical relationship between POP retention and lake properties may allow the calculation of a effect-based maximum load, even though data on diffusion, seepage, sedimentation, resuspension, partitioning coefficients etc. are not available. The problem however is, that there must be an experimental data set for each POP in lake systems before the simplified relation between effect-based maximum load and system properties can be defined and at present these data sets are not available. At this moment the models described in this manual thus seems the best compromise between a relatively accepted description of the behaviour of POPs in surface waters and sediments and a relatively small need for input parameters.

Dynamic models
In comparison to heavy metals in sediment (De Vries, *et al.*, 1998), POPs generally reach a steady-state fairly quickly in the sediment despite their 'persistent' character. Only for POPs that have both a very low degradation potential and adsorb very strongly to the sediment, reaching the steady-state can take a long time. The use of steady-state models for the assessing the risks of POPs in aquatic ecosystems is therefore justified in most cases. Only in cases where the actual load of the POP is varying relatively fast compared to the loss rate by processes such as degradation, steady-state models give a wrong picture of reality. In these cases dynamic models can be useful. If one wants to predict the time period before a certain (critical) limit is reached, they are also useful. Dynamic models for risk assessment of POPs in water and sediment are not presented in this manual.

5.7 The possibilities of calculating PECs and MLs in seas

The calculation methods described in the previous paragraphs are all directed at calculating PECs and effect-based maximum loads for lakes and associated catchment areas. There exists however also large interest in risk assessment methods for seas.
In this paragraph some attention is given to the question whether it is possible to calculate PECS and effect-based maximum loads for seas. The best way to determine whether this is possible, is to analyse the similarities and differences between lakes and seas. The main similarity concerns the fact that in a marine system one can also distinguish between a water compartment, suspended particles and a sediment compartment. Also the processes that determine the behaviour of the pollutant in a marine system are comparable to those in a lake. There is however one big difference between a sea and a lake and that is the degree of

horizontal and vertical homogeneity of the water compartment. Contrary to a (small) lake system, where the assumption of perfect horizontal and vertical mixing is often (but not always) justifiable, one can hardly pretend that this is also the case in a marine system such as the North Sea. Within most marine systems, horizontal currents for example exist that strongly contradict the assumption of horizontal homogeneity. Even in the case that the marine system is polluted by a diffuse source such as atmospheric deposition alone, the resulting concentration pattern will be inhomogeneous due to the various currents within the system boundaries. This means that the methods to calculate PECs or effect-based maximum loads for POPs for lakes, which have been described in the previous paragraphs, are not suitable for calculating PECa or effect-based maximum loads for large aquatic systems like seas.

The question then remains what can be said with respect to the influence of various sources on sea water quality and with respect to the risks that these sources impose on the different parts of the marine ecosystem.

One way to get an understanding of this influence is to folllow the approach applied in the study by Van Pagee and Villars (1994) and by Boon *et al.* (1993). In these studies, information on emissions to the North Sea by rivers, direct discharges, dumping, atmospheric deposition and input from the Baltic Sea and the Atlantic Ocean were compiled and were used as input for marine water and sediment quality models. With these models 2-dimensional concentration patterns in water and sediment were calculated. In Boon *et al.* (1993) the calculated concentration in each grid cell (3.2 x 3.2 km) was related to the various pollution sources in a way that emission reduction percentages could be calculated with respect to individual sources. So with the appropriate marine water and sediment quality models it is possible to calculate PECs in seas but the calculation of effect-based maximum loads in a strict sense is not (yet) possible for seas. It is however shown that emission reduction targets can be derived in some way from model calculations. Of course this requires the access to a marine water and sediment quality model that has the ability to couple the calculated concentrations to the different sources.

6. Input data

6.1 Introduction

In this chapter the input data required for the risk assessment models, that have been described in the previous chapter, are discussed. Collecting the input data is step 4 in both the PEC:PNEC and the AL:ML approaches presented in figure 1.1 in paragraph 1.2. As the value of each input parameter fully depends on the particular characteristics of the considered system and compound, it is not possible to present specific parameter values but it is only possible to present indicative (ranges of) possible values. The input data are divided in compound related input data, water related input data and sediment related input data. Although some input data can not be classified as exclusively water related or sediment related (*e.g.* the data describing the exchange between the water and the sediment), these data are still grouped as predominantly water related and predominantly sediment related. The three groups of input data will be discussed separately. It is furthermore indicated which data is required for the simple models and which is required for the elaborated models.

6.2 Compound related input data

Simple models
For the simple models the following compound related input data are required:

- The critical limits '$[X]_{crit,tot,w}$' and '$[X]_{crit,unc,w}$' in the water compartment and/or '$ctX_{crit,sed}$' in the sediment compartment (for AL:ML approach).
- The actual total load on the lake X_{tl} (for PEC:PNEC approach).
- The adsorption coefficient to organic carbon 'K_{oc}'.
- The factor 'x_{doc}' to account for less efficient adsorption to DOC with respect to adsorption to particulate organic carbon.
- The overall rate constant '$k_{deg,w}$' for degradation in the water compartment.
- The overall rate constant '$k_{deg,sed}$' for degradation in the sediment compartment.
- The mean overall rate constant 'kdeg' for degradation in the catchment.

Elaborated models
Besides the input data mentioned under 'simple models', the following compound related input data are required for the elaborated models:

- Henry's law constant 'K_h'.
- The mass transfer coefficients between water and air 'k_{atm}' and 'k_w'.
- The molecular diffusivity '$D_{mol,w}$' in the water phase.

6.2.1 General discussion of compound related input data

Critical limits

The critical limits in water and sediment are discussed in chapter 4 and will therefore not be addressed here.

Total load

The determination of the actual total load on the lake discussed in Chapter 3 and will therefore not be addressed here.

Adsorption coefficient

The adsorption coefficient K_{oc} is a often experimentally determined parameter of many organic compounds. If it is not known from measurements, it can be estimated assuming a relation between the K_{oc} ($l.kg^{-1}$) and the octanol/water partition coefficient K_{ow} (-). A simple and frequently used equation is given by Karickhoff (1981):

$$K_{oc} = 0.411 \times K_{ow} \qquad (6.1)$$

Factor x_{doc}

Comparison of measured values of adsorption constants for DOC (K_{doc}) and for particulate organic carbon (K_{oc}) gives information on the value of x_{doc}. From measurements on chlorobenzenes and PCBs it appears that x_{doc} has a value of 0.2 for these compounds (Ten Hulscher, 1989).

Degradation rate in water

In the water compartment degradation can be the result of photolysis in the surface layer, hydrolysis or biodegradation. As the rates of these processes strongly depend on the compound and the environmental characteristics (amount of incoming solar radiation, presence of biodegrading organisms), it is difficult to give general indications of the degradation rate in water. Experimentally determined values are therefore essential.

Degradation rate in sediment

In the sediment compartment hydrolysis and biodegradation are the main degradation processes. For the same reasons as mentioned above, experimentally determined values are essential.

Degradation rate in the catchment

The degradation rate in the catchment, as used in the calculation, is in essence a parameter for the combined degradation processes in the soils and waters of the catchment area. It is therefore a difficult parameter to estimate. Estimations should be based on what is known of the above mentioned degradation rates in water and sediment and in soil.

Henry's law constant

Henry's law constant K_h is an often experimentally determined property of organic compounds. If it is not known from measurements, it can be estimated from the compounds solubility and saturated vapour pressure according to:

$$K_h = \frac{P_s \times M}{R \times T \times S} \qquad (6.2)$$

where:

P_s = the saturated vapour pressure (Pa)
M = the molecular weight ($g.mol^{-1}$)
R = the gas constant ($Pa.m^3.K^{-1}.mol^{-1}$)
T = the temperature (K)
S = the solubility ($g.m^{-3}$)

Mass transfer coefficients

The mass transfer coefficient k_{atm} in the air and k_w in the water at the air-water interface depend mainly on the ambient wind speed. To give an impression of a possible values for the transfer coefficients, the values used by Mackay *et al.* (1985) in calculating the diffusive exchange between water and air are given: $1.39.10^{-3}$ $m.s^{-1}$ for k_{atm} and $1.39.10^{-5}$ $m.s^{-1}$ for k_w.

Molecular diffusivity in water

Molecular diffusion in the water phase is slow compared to molecular diffusion in the gas phase. As a rule of thumb it can be assumed that diffusion in water is 1000 times slower than in air. The molecular diffusivity in air depends on the molecular weight of the compound and the temperature. An example of an empirically determined relation between these properties is given by Huygen *et al.* (1986):

$$D_{mol,g} = 8.8 \,.\, 10^{-9} \times (1000 \times R \times T / M)^{0.66} \qquad (6.3)$$

where:

$D_{mol,g}$ = the molecular diffusivity in the gas phase ($m^2.s^{-1}$)
R = the gas constant ($8.31\ J.K^{-1}.mol^{-1}$)
T = the temperature (K)
M = the molecular weight ($g.mol^{-1}$)

Of course other estimation methods for the diffusivity in air and water exist (Lyman *et al.*, 1982) and can equally well be applied.

6.3 Data related to the water compartment

Simple models
For the simple models the following water related input data are required:

- The mass flow of water 'Q_l' through the lake.
- The surface areas 'A_l' and A_c' of the lake and catchment.
- The mean residence time 't' in the catchment area.
- The depth 'z_w' of the water compartment.
- The concentration of suspended particles 'sus' in the water.
- The fraction organic carbon '$fr_{oc,sus}$' in suspended particles.
- The concentration of dissolved organic carbon 'DOC_w' in the water.

Elaborated models
Besides the input data mentioned under 'simple models', the following compound related input data are required for the elaborated models:

- The flux of water 'Fsp' seeping through the sediment.

6.3.1 General discussion of water related input data

Flow of water
The flow of water Q_l through a lake may range from no flow in completely isolated lakes to several hundreds or even thousands of cubic metres per second in lakes that are fed by large rivers.

Surface area
The surface areas A_l and A_c of the lake and catchment under consideration may vary from very small such as in the case of a local mere (for example 1000 m^2) to large in the case of large lakes that may be as large as 1000 km^2. The upper limit of the size of the lake for which a effect-based maximum load can be calculated is in fact determined by the limits of validity of the assumption of homogeneous mixing on the time scale of reaching a steady-state.

Mean residence time
The mean residence time of a POP in the catchment area predominatly depends on the size of the catchment area, on the soil types in the catchment area and on the sorption characteristics of the POP under consideration. It is therefore difficult to give an indications of possible mean residence times. Besides model calculations with combinations of soil models and aquatic models for the catchment , tests with tracers can give an indication of the residence time.

Depth of the water compartment
The depth z_w of the water compartment under consideration depends of course on the type of surface water. In case of a mere, a depth of 0.5-1.0 m is likely whereas large

lakes may have depths of 10 m or more. Again the upper limit of the depth of the aquatic system for which a effect-based maximum load can be calculated is in fact determined by the limits of validity of the assumption of vertical mixing on the time scale of reaching a steady-state.

Concentration of suspended particles
The concentration of suspended particles sus in the water compartment depends on the composition of the sediment layer and on turbulency of the water which in turn depends on wind speed and water flow velocity. The concentration may therefore vary within broad ranges and also depends on the averaging time that is considered. Possible values range from 1 to 100 mg/l.

Organic carbon content of suspended particles
The organic carbon content of suspended particles $fr_{oc,sus}$ depends on the source of the particles. In some cases the suspended particles mainly consist of clay and silt particles containing few organic matter, in other cases the suspended particles may mainly consist of organic matter. The value may therefore range from 0.01 to 0.6 $kg.kg^{-1}$. In the latter case the particles consist of pure organic matter.

Dissolved organic carbon
The concentration of dissolved organic carbon DOC in water depends on the properties of the sediment and the origin of the water. The concentration of DOC in non-humic surface waters generally ranges between 1 and 20 $mg.l^{-1}$. In humic brown waters, DOC concentrations may however be as large as 60 $mg.l^{-1}$ (Bishop *et al.*, 1996; Kortelainen and Saukkonen, 1996).

Water seeping through the sediment
Whether water from the water compartment seeps through the sediment compartment depends on several factors of which differences in water pressure and water conductivity of the sediment and underlying layer are the most important. Water in canals that are situated higher that the environment may seep through the sediment and pass underneath the dikes to the polder. In other cases it is however possible that water enters a water compartment by welling up through the sediment. Seepage thus may vary from zero (or even negative values) to several meters water per year. Negative value can however not be handled in the effect-based maximum load calculation method.

6.4 Data related to the sediment compartment

Simple models
For the simple models the following sediment related input data are required:
For the calculation of PEC in water or ML based on critical limit in water:
- The dry bulk density 'ρ_{sed}' of the sediment.
- The net sedimentation flux 'F_{netsed}'.

Additionally for the calculation of PEC in sediment or ML based on critical limit in sediment:

- The depth 'z_{sed}' of the sediment compartment.
- The fraction organic carbon '$fr_{oc,sed}$' in the sediment.
- The concentration of dissolved organic carbon 'DOC_{pw}' in the porewater.

Elaborated models

Besides the input data mentioned under 'simple models', the following compound related input data are required for the elaborated models:

- The porosity 'p' of the sediment.
- The sedimentation flux 'F_{sed}' and the resuspension flux 'F_{res}'.
- The diffusion path length 'z_{dif}' in the sediment at the water-sediment interface.

6.4.1 General discussion of sediment related input data

Dry bulk density of the sediment

The dry bulk density of the sediment depends on the specific gravity of the sediment particles and the porosity of the sediment. If the sediment predominantly consist of silicates which have a specific gravity of 2750 $kg.m^{-3}$ and the sediment has a porosity of 0.5 $m^3.m^{-3}$, then the dry bulk density is 1375 $kg.m^{-3}$.

Net sedimentation flux

The sedimentation and resuspension fluxes in aquatic systems depend on several parameters of which turbulence in the water compartment is probably the most important one. In many aquatic systems sedimentation and resuspension alternate in time as a result of varying water flow or wind speed. In these cases net sedimentation or resuspension is only discernable on somewhat longer timescales. Alternating but equal sedimentation and resuspension fluxes result in exchange of pollutant between the water and sediment compartment. Net sedimentation results in burial of sediment and the pollutant within it. Net sedimentation may vary from less than 1 $mm.yr^{-1}$ to more than 25 $mm.yr^{-1}$.

Depth of the sediment compartment

The mixing depth of the sediment compartment depends on the intensity of the sedimentation and resuspension process and of the amount of bioturbation in the sediment. A often used but rather arbitrarily chosen mixing depth is 0.1 m.

Organic carbon content of the sediment

As with the suspended particles, the organic carbon content of the sediment depends on the source of the particles. In some cases the sediment will mainly consist of clay, silt and sand particles containing few organic carbon, in other cases the sediment will contain a substantial amount of organic carbon. The value

may therefore range from 0.01 to 0.6 $kg.kg^{-1}$. In the latter case the particles consist of pure organic matter.

Dissolved organic carbon in the pore water
The DOC concentration in the pore water of the sediment mainly depends on the properties of the sediment such as the particulate organic matter content, the type of organic matter and the pH. Information on the DOC concentration in porewater is not readily available in the literature. As a first approximation one may assume that the DOC concentration in porewater and surface water are equal.

Porosity of the sediment
The porosity of the sediment depends on the amount of compaction after sedimentation but will in many cases be approximately 0.5 $m^3.m^{-3}$.

Sedimentation and resuspension fluxes
See 'net sedimentation flux'.

Diffusion path length in the sediment
The diffusion path length in the sediment, necessary in order to calculate the diffusive exchange between the water and sediment compartments, is difficult to estimate. In many models the diffusion path length is assigned a value equal to half the thickness of the uppermost sediment layer. However, in case of sediments with large mixing depths this may lead to values that are too high. In case of a mixing depth of 10 cm, a value of 2.5 cm to 5 cm for the diffusion path length is often used.

7. Sources of uncertainty

7.1 Introduction

The uncertainty in the calculation of concentrations and effect-based maximum loads is mainly determined by (Kros *et al.*, 1993):

1. The uncertainty in the critical limits for the receptor.
2. The uncertainty in the calculation methods (model structure and model implementation).
3. The uncertainty in the input data (model input, parameters and initial state of variables) due to spatial variability and lack of knowledge.

These three sources of uncertainty are discussed in the following paragraphs.

7.2 Critical limits

The critical limits for aquatic ecosystems suffer from several uncertainties. The most important are discussed below.

Safety factors
The main uncertainty in deriving critical limits with the modified EPA method (see paragraph 4.2) is in the fact that the value of such a critical limit is partly based on safety factors which have no scientific underpinning. These safety factors, with values between 10 and 1000, account for translating acute toxicity data to chronic no effect levels, for using QSARs instead of experimental data and for a low amount of available data.

Extrapolation procedure
A major reason for uncertainties in critical limits for POPs is related to the extrapolation procedure of single species toxicity data to a critical value that is assumed to protect an ecosystem sufficiently. Use of extrapolation models, such as given by Aldenberg and Slob (1991) (see paragraph 4.2) are based on the assumption that (Witter, 1992; Forbes and Forbes, 1993; Smith and Cairns, 1993):

1. The distribution of species sensitivities in natural ecosystems approximates a postulated theoretical distribution (*e.g.* log-normal or log-logistic).
2. The (sensitivities of) species used in laboratory tests are a random choice of species form all organisms in an ecosystem, thus providing an unbiased measure of the mean and variance of the sensitivity distribution of species in that ecosystem.
3. The observed variation in toxicity data is entirely due to variation in POP sensitivity between species.

4. Interactions among species in ecosystems can be ignored.

The validity of all these assumptions is questionable or even not true, since (Witter, 1992; Forbes and Forbes, 1993; Smith and Cairns, 1993):

1. Toxicity data are generally too few to postulate a distribution.
2. It is unlikely that test species are random choices.
3. Laboratory and field conditions, such as organic matter content, influence POP availability.
4. There are interactive effects.

Effect of organic matter content on POP availability and toxicity can be accounted for in deriving critical limits. Apart form using No Observed Effect Concentrations (NOECs), several authors (*e.g.* Witter, 1992; Tyler, 1992) use Lowest Observed Effect Concentrations (LOECs). Both values can lead to bias, especially when the LOEC value corresponds to the lowest level of POP addition in the experiment and the NOEC to the highest level of POP addition in another experiment. Considering the uncertainties in statistical extrapolation, Forbes and Forbes (1993) state that use of an arbitrary safety factor of *e.g.* 10 or 100 is more appropriate at the moment.

In summary, it is important to note that differences in the literature with respect to critical limits are due to:

1. Different effects or species are considered.
2. Different extrapolation methods are used.
3. Different laboratory or field conditions are involved.

Time-scale and averaging depth

It is often not clear for which time-scale a critical limit is supposed to be valid. It makes, for example, a large difference if a critical limit is supposed to be met at any moment or that temporary exceedances are permitted, provided the annually averaged concentration is not exceeded. The same uncertainty applies to the averaging depth for which the critical limit for sediments is meant to be valid. Should the concentration in the sedimentl stay below the critical value even in the uppermost centimetre or is exceedance accepted, provided that the concentration averaged over 10 cm depth does not exceed the critical limit?

7.3 Calculation methods

The proposed models for the risk assessment of POPs in aquatic ecosystems are based on a number of assumptions. The main assumptions are:

1. The concentration of the POP in the aquatic system (including the sediment compartment) has reached a steady-state.
2. The POP present in the system follows the concept of equilibrium partitioning.
3. Both the water compartment and the sediment compartment are homogeneously mixed.
4. The sedimentation flux at least equals the resuspension flux.
5. Degradation of the POP in both the surface water, the sediment and the catchment area can be described by a first order equation.

As the validity of the calculation method is mainly determined by the validity of these assumptions, they are discussed below.

Steady-state

The assumption of steady-state implies that the concentration in the aquatic system does not change in time because the amount of POP entering the system is equal to the amount that leaves the system. The validity of this assumption depends, just as in the case of the soil system, on the magnitude of the time-scales of the various input, output and exchange processes. The exchange of POP between the water and sediment compartments for example is often much slower than the input of POP in the water compartment by lateral inflow.
If in such a case the input of POP changes, it takes some time before the steady-state has recovered, which may cause problems in calculating the PEC or effect-based maximum load of for example a pesticide that is emitted in only a small part of the year. In other words: If the time-scale of reaching the steady-state is much longer than the time-scale of changes in the input or output processes it is difficult to compare an actual load on the system with a effect-based maximum load or a PEC with a PNEC.

Equilibrium partitioning

The assumption of equilibrium partitioning in an aquatic system means that it is assumed that a POP in the water compartment partitions over the dissolved phase and the adsorbed phase of suspended particles and that a POP in the sediment compartment partitions over the pore water (dissolved) phase and the adsorbed phase of the sediment. In both cases it is assumed that the concentration in each of these phases is in a state of equilibrium at any moment. As in the case of equilibrium partitioning in a soil system it can be stated that the concept of equilibrium partitioning is often employed to describe the distribution of organic pollutants in aquatic systems. This does however not mean that the concept of equilibrium partitioning has unlimited validity: Irreversible sorption and desorption rates that are not equal may cause behaviour of the POP in the aquatic system that deviates from the modelled behaviour. As however hardly any quantitative or even qualitative information is available on the significance of these phenomena, it is difficult to incorporate them in the calculation of PEC or effect-based maximum load. For the same reasons is adsorption in the calculation

method described as sorption to particulate organic matter only and are sorption to other adsorbents not taken into account.
Further it must be remarked that using the K_{om} to describe the process of equilibrium partitioning implies that the method is only valid for lipophilic, non-ionic organic compounds.

Homogeneously mixed
It is assumed that both the water compartment and the sediment compartment are homogeneously mixed. Due to this, system properties and concentrations of the pollutant do not show horizontal or vertical variation within the compartments. Although water is relatively easily mixed, this does not mean that the assumption of homogenous mixing is valid at all times and in all situations. In general it can be remarked that homogeneous mixing does apply less to very large surface waters, such as seas, than to smaller surface waters, such as small lakes. It does however depend on the requested amount of detail, both in time and space, whether the inaccuracy associated with the assumption of homogeneous mixing is acceptable or not. In all cases, PECs or effect-based maximum loads calculated on the assumption of homogeneous mixing are more suitable to be compared to diffuse sources such as atmospheric deposition than to point sources.

Sedimentation/resuspension
The models to calculate the PEC or the effect-based maximum load that are presented in this manual are restricted to aquatic systems in which the sedimentation flux at least equals the resuspension flux. This is the consequence of the fact that when the resuspension flux would be greater that the sedimentation flux, the sediment layer would eventually disappear or the considered sediment layer would move deeper and deeper. In the last mentioned case, one has no information on the unburied sediment quality so the calculation becomes inaccurate.

First order degradation
In the calculation methods the loss by chemical and biological degradation is described by a first order loss equation. From experiments it is however known that organic compounds do not always exhibit first order biodegradation kinetics. Possible other kinetics include zero order, logistic and logarithmic kinetics. In principle one should know the concentration of the POP and the biodegrading cell density in the water or sediment before one can decide which kinetic model is valid for the specific conditions. In most cases, especially in the more generic studies, this information is however not available. As the first order model is valid for situations where the POP concentration is too low to allow for growth of the biodegrading population (Alexander and Scow, 1989), this model is probably the best choice in those cases where the load of POP on the aquatic system is relatively low (for example where atmospheric deposition is the only source of pollution). Another reason to choose the first order model is a more practical one

as most information on the biodegradation rate of POPs is presented in the literature as a first order degradation rate or half-life.

7.4 Input data

Although the value of every single input parameter inevitably carries an amount of uncertainty, it is believed that especially the uncertainty in the degradation rate of organic compounds can be the cause of large uncertainties in the calculation of PECs and effect-based maximum loads. In many cases degradation is the main loss process from the aquatic system (other then lateral outflow), so every change in the assumed value of the degradation rate has a clear effect on the PEC or effect-based maximum load.
Especially in the more generic studies it is difficult to assign the degradation rate a value that has general validity. If the effect-based maximum load has to be calculated for a specific site with known characteristics this is a smaller problem. Further it must be realised that for example compound properties that are deduced from other properties can contain rather large uncertainties. Other input data that are often uncertain, especially in the case of more generic studies, include water and sediment related parameters such as the mixing depth.
Due to the uncertainties in the input data for the water/sediment model, it is advisable to perform some sort of sensitivity analysis and/or uncertainty analysis when calculating effect-based maximum loads for surface waters. In this way one can get an idea of the range of uncertainty in the PEC or effect-based maximum load itself.

8. References

Aldenberg, T. and W. Slob, 1991.
Confidence limits for hazardous concentrations based on logistically distributed NOEC toxicity data. RIVM report nr. 719102002.

Aldenberg, T. and W. Slob, 1993.
Confidence limits for hazardous concentrations based on logistically distributed NOEC toxicity data. Ecotoxicology and Environmental Safety, vol. 25, pp. 48-63.

Alexander, M. and K.M. Scow, 1989.
Kinetics of biodegradation in soil. In: Reactions and movement of organic chemicals in soils. SSSA Special Publication, no. 22, pp. 243-269.

Bakker, D.J., 1995.
The influence of atmospheric deposition on soil and surface water quality in The Netherlands. MW-TNO report nr. R 95/013, Delft, The Netherlands.

Bakker, D.J. and W. de Vries, 1996.
Manual for calculating critical loads of persistent organic pollutants for soils and surfaces waters. Preliminary guidelines for environmental quality criteria, calculation methods and input data. TNO-MEP report nr. R96/509, Delft, The Netherlands.

Bakker, D.J. and W. de Vries, 1998.
Effect-based approaches for persistent organic pollutants in surface waters. Overview methods/models - POPs water. In: Proceedings of the UN-ECE CLRTAP TF Mapping Workshop on Critical Limits and Effect-based Approaches for Heavy Metals and POPs, 3-7 November 1997, Bad Harzburg, Germany. UBA report 5/98.

Berdowski J.J.M., Baas J., Bloos J.-P.J., Visschedijk A.J.H., and Zandveld P.Y.J., 1997.
The European Emission Inventory of Heavy Metals and Persistent Organic Pollutants. TNO, Report UBA-FB, UFOPLAN-Ref.No. 104.02 672/03, Apeldoorn, 239 p.

Bishop, K., S. Köhlen and L. Rapp, 1996.
Estimating the pH buffering capacity of dissolved organic carbon from Swedish surface water chemistry inventory data. Water, Air and Soil Poll. (submitted).

Boon, J.G., J.A, van Pagee and D. Jonkers, 1993.
Dealing with risks for marine ecosystems (RISMARE). Modelling study into the sediment quality of the North Sea and Wadden Sea in relation to emissions and environmental quality objectives. Delft Hydraulics report nr. T537, Delft, The Netherlands (in Dutch).

De Vries, W., D.J. Bakker and H.U. Sverdrup, 1998.
Manual for calculating critical loads of heavy metals for aquatic ecosystems. Guidelines for critical limits, calculation methods and input data. DLO Winand Staring Centre, report 165, Wageningen, The Netherlands.

Dutchak, S., W.A.J. van Pul and C.J. Sliggers, 1998.
Emissions, modelling and measurements of heavy metals and persistent organic pollutants. In: Proceedings of the UN-ECE CLRTAP TF Mapping Workshop on Critical Limits and Effect-based Approaches for Heavy Metals and Persistent Organic Pollutants. Bad Harzburg, Germany, 3-7 November 1997. UBA report 5/98.

EPA, 1984.
Estimating concern levels for concentration of chemical substances in the environment. EPA, Environmental Effects Branch, Washington, USA.

Everts, J.W., M.M. Ruys, E.J. van de Plassche, J, Pijnenburg, R. Luttik, J. Lahr, H. van der Valk and J.H. Canton, 1992.
Secondary poisoning in the food chain. A way to derive maximum acceptable concentrations in the marine environment. DGW/RIVM (in Dutch).

Forbes, T.L. and V.E. Forbes, 1993.
A critique of the use of distribution-based extrapolation models in ecotoxicology. Functional Ecology, vol. 7, pp249-254.

Galperin, M. and A. Maslyaev, 1996.
A tentative version of airborne transport POP model. Description and preliminary results of sensitivity studies. EMEP/MSC-E report 3/96.

Gobas, F.A.P.C., D.C.G. Muir and D. Mackay, 1988.
Dynamics of dietary bioaccumulation and faecal elimination of hydrophobic organic chemicals in fish. Chemosphere, vol. 17, pp 943-962.

Huygen, C., J.A. Duiser and L. de Vries, 1986.
Emission of pesticides to the air during spraying of low crops. Estimation methods for concentrations and deposition fluxes in the vicinity. MT-TNO report R86/227, Delft, The Netherlands (in Dutch).

Jacobs, C.M.J. and W.A.J. van Pul, 1996.
Long-range transport of persistent organic pollutants,I: Description of surface-atmosphere exchange modules and implementation in EUROS. RIVM report 722401013.

Jury, W.A., W.F.Spencer and W.J.Farmer, 1983.
Behavior Assessment Model for Trace Organics in Soil:I Model description. J. Environ. Qual.,12, 558-564.

Karickhoff, S.W., 1981.
Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. Chemosphere vol. 10, nr. 8, pp. 833-846.

Kortelainen. P and S. Saukkonen, 1996.
Trends in organic versus anthropogenic acidity in finnish streams. Water Air and Soil Poll. (submitted).

Kros, J., W. De Vries, P. Janssen and C. Bak, 1993.
The uncertainty in forecasting regional trends of forest soil acidification. Water, Air and Soil Pollution, vol. 66, pp. 29-58.

Liss, P.S. and P.G. Slater, 1974.
Flux of gases across the air-sea interface. Nature, vol. 247, pp. 181-184.

Lyman, W.J., W.F. Reehl and D.H. Rosenblatt (eds.), 1982.
Handbook of chemical property estimation methods. McGraw-Hill Book Company.

Mackay, D., 1982.
Correlation of bioconcentrations factors. Environ. Sci. Technol., vol. 16. pp.274-278.

Mackay, D., S. Paterson, B. Cheung and W. Brock Neely, 1985.
Evaluating the environmental behaviour of chemicals with a level III fugacity model. Chemosphere, vol. 14, no. 3/4, pp. 335-374.

MSC-E, 1997.
Progress report, 1997. Modelling of long-range transport of lindane and PCB-153 with implementation of RIVM module on atmosphere-surface exchange.

OECD, 1992.
Report of the OECD workshop on the extrapolation of laboratory aquatic toxicity data to the real environment. OECD Environment Monographs no. 59., Paris, France.

Pekar, M, 1996.
Regional models LPMOD and ASIMD. Allgorithms, parameterization and results of application to Pb and Cd on European scale for 1990. EMEP/MSC-E report 9/96.

Romijn, C.A.F., R. Luttik, D. v.d. Meent, W. Slooff and J.H. Canton, 1993.
Presentation of a general algorithm to include effect assessment on secondary poisoning in the derivation of environmental quality criteria. Part 1: Aquatic food chains. Ecotox. Env. Safety, vol. 26, pp 61-85.

Ruys, M.M. and J. Pijnenburg, 1991.
Method and calculation of maximum accepted risk levels in the aquatic environment of wading-birds and sea-birds. AIDEnvironment (in Dutch).

Sliggers, C.J. and H.H. Jager, 1993.
Matrix International Working Groups/Task Forces on Heavy Metals and Persistent Organic Pollutants. Ministry of VROM, Directorate General for Environmental Protection, The Hague, The Netherlands.

Smith, E.P. and J. Cairns, 1993.
Extrapolation methods for setting ecological standards for water quality: statistical and ecological concerns. Ecotoxicology, vol. 2, pp. 203-219.

Ten Hulscher, Th.E.M., 1989.
Estimation of the concentration of some micro-pollutants in the sediments of the Volkerakmeer and Zoommeer. RIZA report nr. 89.050, Lelystad, The Netherlands (in Dutch).

Thomann, R.V., 1981.
Equilibrium model of fate of microcontaminants in diverse aquatic food chains. Can. J. Fish. Aquat. Sci., vol. 38, pp. 280-296.

Thomann, R.V., 1989.
Bioaccumulation model of organic chemical distribution in aquatic food chains. Environ. Sci. Technol., vol. 23, pp. 699-707.

Tyler, G., 1992.
Critical concentrations of heavy metals in the mor horizon of Swedish forests. Swedish Environmental Protection Agency, report 4078, Solna, Sweden,

Van de Meent, D. , T. Aldenberg, J.H. Canton, C.A.M. van Gestel and W. Slooff. 1990.
Desire for levels. Background study for the policy document "Setting environmental quality standards for water and soil". RIVM report no. 670101002.

Van den Hout, K.D. (ed.), 1994.
The impact of atmospheric deposition of non-acidifying pollutants on the quality of European forest soils and the North Sea. Main report of the ESQUAD project. IMW-TNO report nr. R 93/329, Delft, The Netherlands.

Van den Hout, K.D., D.J. Bakker, J.J.M. Berdowski, J.A. van Jaarsveld, G.J. Reinds, J. Bril, A. Breeuwsma, J.E. Groenenberg, W. de Vries, J.A. van Pagee, M. Villars and C.J. Sliggers, 1998.
The impact of atmospheric deposition of non-acidifying substances on the quality of European forest soils and the North Sea. Accepted for publication in Water, Air and Soil Pollution.

Van de Plassche, E.J., 1994.
Towards integrated environmental quality objectives for several compounds with a potential for secondary poisoning. RIVM report no. 679101012.

Van de Plassche, E.J., V. Bashkin, R. Guardans, K. Johansson and J. Vrubel, 1998.
An overview of critical limits for heavy metals and POPs. In: Proceedings of the UN-ECE CLRTAP TF Mapping Workshop on Critical Limits and Effect-based Approaches for Heavy Metals and Persistent Organic Pollutants, 3-7 November 1997, Bad Harzburg, Germany. UBA-report 5/98.

Van Jaarsveld, J.A, 1994.
Atmospheric deposition of cadmium, copper, lead, benzo (a) pyrene and lindane over Europe and its surrounding marine areas. Background report of the ESQUAD project. RIVM, report 222401002, Bilthoven, The Netherlands.

Van Jaarsveld, J.A., W.A.J. van Pul and F.A.A.M. de Leeuw, 1997.
Modelling transport and deposition of persistent organic pollutants in the European region. Atmospheric Environment. *In press.*

Van Pagee, J.A. and M.T. Villars, 1994.
Influence of atmospheric deposition on the North Sea and Continental Shelf. Background report of the ESQUAD project. Delft Hydraulics report nr. T1010, Delft, The Netherlands.

Van Pul, W.A.J., J.A van Jaarsveld and F.A.A.M. de Leeuw, 1996.
Modelling of the atmospheric long-range transport and deposition of POP over Europe. Background document presented at the EMEP workshop on the assessment of EMEP activities concerning heavy metals and persistent organic pollutants and their further development, 24-26 September 1996, MSC-E Moscow, Russian Federation.

Van Pul, W.A.J., F.A.A.M. de Leeuw, J.A. van Jaarsveld, M.A. van der Gaag and C.J. Sliggers. 1998.
The potential for long-range transboundary atmospheric transport. Chemosphere, vol. 37, pp. 113-141.

Van Straalen, N.M. and C.A.J. Denneman, 1989.
Ecotoxicological evaluation of soil quality criteria. Ecotox. Environ. Safety, vol. 18, pp. 214-251.

Vollenweider, R.A., 1975.
Input-Output models. With special reference to the phosphorus loading concept in limnology. Hydrology 37, vol. 1, pp. 53-84.

Vollenweider, R.A., 1976.
Advances in defining critical loading levels for phosphorus in lake eutrophication. Mem. Ist. Ital. Idrobiol. vol. 33, pp. 53-83.

Witter, E., 1992.
Heavy metal concentrations in agricultural soils critical to micro-organisms. Swedish Environmental Protection Agency, report 4079, Sweden.

Authentication

Name and address of the principal:

Ministry of Housing, Spatial Planning and the Environment
Directorate-General for Environmental Protection
P.O. Box 30945
2500 GX The Hague

Names and functions of the cooperators:

D.J. Bakker	Project Leader; TNO Institute of Environmental Sciences, Energy Research and Process Innovation, Den Helder, The Netherlands
W. de Vries	Research Scientist; DLO Winand Staring Centre, Wageningen, The Netherlands
E.J. van de Plassche	Research Scientist; National Institute of Public Health and the Environment , Bilthoven, The Netherlands
W.A.J. van Pul	Research Scientist; National Institute of Public Health and the Environment , Bilthoven, The Netherlands

Date upon which, or period in which, the research took place:

September 1996 - December 1998

Signature:

D.J. Bakker
Project Leader
7 December 1998

Approved by:

M.C.Th. Scholten
Head of Department
7 December 1998

Annex 1 Critical limits in UN-ECE countries

In this annex an overview of critical limits of POPs in surface waters, sediment, drinking water and fish that are operational in various UN-ECE countries is presented. The overview is adapted from Van de Plassche *et al.* (1998) who made the inventory of critical limits as a starting point for discussions on the Workshop on Critical Limits and Effect-based Approaches for Heavy Metals and Persistent Organic Pollutants, Bad Harzburg, Germany, 3-7 November 1997. In this annex only the numerical values of the critical limits are given. For information on the terminology, consequences, status, focus on specific functions and scientific basis of the systems in the distinguished countries, the reader is referred to Van de Plassche *et al.* (1998). Most of the critical limits presented are based on an effect-based approach: they are derived to prevent either effects on the ecosystem or effects on human beings. However not many of them will be derived by taking into account the possibility of secondary poisoning. It is therefore advised not to use any of the presented limits without proper knowledge of the way of deriving the limits.
The POPs are grouped in 4 groups with different priorities in international environmental protection policies (Van de Plassche *et al,*1998).

References

Van de Plassche, E.J., V. Bashkin, R. Guardans, K. Johansson and J. Vrubel, 1998. An overview of critical limits for heavy metals and POPs. In: Proceedings of the UN-ECE CLRTAP TF Mapping Workshop on critical limits and effect-based approaches for heavy metals and persistent organic pollutants, 3-7 November 1997, Bad Harzburg, Germany. UBA-report 5/98.

Belarus, Moldavia, Russia, Ukraine	Fresh water MPC (µg/l)	Fresh water IAL (µg/l)	Sediment (mg/kg)
First priority			
benzo(b)fluoranthene			
benzo(k)fluoranthene			
benzo(ghi)perylene			
benzo(a)pyrene	0.005		0.02
fluoranthene			
hexachlorobenzene	50		
indeno(1,2,3-cd)pyrene			
TCDD	200 (furans)	0.035 (doxins)	
Second priority			
PCBs		100	
pentachlorophenol	10		
lindane		4	0.1
Third priority			
chlordane			
endosulfan			
fenthion			
nitrofen	60		
tetrachloroethene			
toxaphene		5	
trichlorobenzene	30		
trichloroethylene		30	
trichloromethane		50	
xylene			
Fourth priority			
aldrin	2		
chlordecone			
dieldrin			
DDT	100		0.1
endrin			
heptachlor	50		
hexabromobiphenyl			
mirex			
short chain chlor. paraffins			

MPC is Maximum Permissible Concentration

IAL is Interim Acceptable Level

Bulgaria	Surface water (I) (µg/l)	Surface water (II) (µg/l)	Surface water (III) (µg/l)	Drinking water (µg/l)
First priority				
benzo(b)fluoranthene				
benzo(k)fluoranthene				
benzo(ghi)perylene				
benzo(a)pyrene				
fluoranthene				
hexachlorobenzene				
indeno(1,2,3-cd)pyrene				
TCDD				
Second priority				
PCBs				
pentachlorophenol				
lindane				
Third priority				
chlordane				
endosulfan				
fenthion				
nitrofen				
tetrachloroethene				
toxaphene				
trichlorobenzene				
trichloroethylene				
trichloromethane				
xylene	0.1	0.1	2	
Fourth priority				
aldrin	0.2	0.2	0.2	0.002
chlordecone				
dieldrin				
DDT				
endrin				
heptachlor				
hexabromobiphenyl				
mirex				
short chain chlor. paraffins				

Canada	Fresh water (µg/l)	Sediment fresh TEL (mg/kg)	Sediment fresh PEL (mg/kg)	Sediment marine TEL (mg/kg)	Sediment marine PEL (mg/kg)	Drinking water (µg/l)
First priority						
benzo(b)fluoranthene						
benzo(k)fluoranthene						
benzo(ghi)perylene						
benzo(a)pyrene		0.039	0.782	0.089	0.763	0.01
fluoranthene		1.113	2.535	0.113	1.494	
hexachlorobenzene	0.0065					
indeno(1,2,3-cd)pyrene						
TCDD						
Second priority						
PCBs	0.001 (total)	0.034	0.277			
pentachlorophenol	0.5					60; <=30
lindane		0.0009	0.0014	0.0003	0.0010	4
Third priority						
chlordane	0.006	0.0045	0.0089	0.0023	0.0048	7
endosulfan	0.02					
fenthion						
nitrofen						
tetrachloroethene	110					
toxaphene						
1,2,3 trichlorobenzene	0.9					
1,2,4 trichlorobenzene	0.5					
1,3,5 trichlorobenzene	0.65					
trichloroethylene	20					50
trichloromethane	2					100
xylene						
Fourth priority						
aldrin	0.004					0.7
chlordecone						
dieldrin	0.004	0.0029	0.0667	0.0007	0.0043	0.7
DDT	0.001	0.0070	4.45	0.0039	0.0517	30
endrin	0.0023	0.0027	0.0624			0.2
heptachlor	0.01	0.0006	0.0027			3
mirex						
short chain chlor. paraffins						

Drinking water: parameters for aesthetic objectives are denoted with <=

TEL: threshold effect level aquatic life, draft interim quality guideline; PEL: probable effect level aquatic life.TEL and PEL for heptachlor are values for heptachlor epoxide.

DDT drinking water: total all isomers.

Croatia	Surface water wat. sources (µg/l)	Surface water irrig./indus. (µg/l)	Coastal water wat. sources (µg/l)	Coastal water irrig./indus. (µg/l)	Drinking water (µg/l)
First priority					
benzo(b)fluoranthene					200
benzo(k)fluoranthene					200
benzo(ghi)perylene					200
benzo(a)pyrene					200
fluoranthene	5	50	5	10	200
hexachlorobenzene	1	1	1	1	
indeno(1,2,3-cd)pyrene					200
TCDD	4.5E-7	4.5E-7	4.5E-7	4.5E-7	
sum PAH					1000
Second priority					
PCBs	0.001	0.01	0.001	0.01	
pentachlorophenol	1	10	1	10	
lindane	0.01	0.1	0.004	0.04	
Third priority					
chlordane	0.01	0.1	0.001	0.04	
endosulfan					
fenthion					
nitrofen					
tetrachloroethene	2	15	2	15	
toxaphene	0.005	0.05	0.005	0.05	
trichlorobenzene	10	20	10	20	
trichloroethylene	20	75	20	20	
trichloromethane					
xylene	50	100	50	100	
Fourth priority					
aldrin	0.003	0.02	0.003	0.02	
chlordecone					
dieldrin	0.003	0.03	0.003	0.03	
DDT	0.001	0.01	0.001	0.01	
endrin	0.004	0.04	0.004	0.04	
heptachlor	0.001	0.01	0.001	0.01	
hexabromobiphenyl					
mirex					
short chain chl. paraffins					

Czech republic	Surface water water sources (µg/l)	Surface water other sources (µg/l)	Sediment (mg/kg)	Human food (mg/kg fw)	Drinking water (µg/l)
First priority					
benzo(b)fluoranthene				0.002	
benzo(k)fluoranthene				0.002	
benzo(ghi)perylene					
benzo(a)pyrene	0.01	0.05		0.002	0.01
fluoranthene					0.04
hexachlorobenzene					
indeno(1,2,3-cd)-pyrene					
TCDD					
sum PAH				0.02	40
sum chlor. pesticides					
chlorinated pesticide					
chlorobenzenes	3	10			3
chlorophenols					
Second priority					
PCBs		0.025	0.2		0.05
pentachlorophenol					
lindane					
Third priority					
chlordane					
endosulfan					
fenthion					
nitrofen					
tetrachloroethene					
toxaphene					
trichlorobenzene					
trichloroethylene					
trichloromethane					
xylene					
Fourth priority					
aldrin					
chlordecone					
dieldrin					
DDT					
endrin					
heptachlor					
hexachlorobiphenyl					
mirex					
short chain chlor. parafins.					

Denmark	Surface water (µg/l)	Drinking water (µg/l)
First priority		
benzo(b)fluoranthene		
benzo(k)fluoranthene		
benzo(ghi)perylene		
benzo(a)pyrene		
fluoranthene		
hexachlorobenzene		
indeno(1,2,3-cd)pyrene		
TCDD		
sum PAKs	1	
Second priority		
PCBs	0.01	
pentachlorophenol	1	0.01
lindane	0.01	
sum other chlorophenols than PCP	0.01	0.1 (including PCP)
phenols		0.5
Third priority		
chlordane	0.004	
endosulfan	0.0001	
fenthion	0.01	
nitrofen		
tetrachloroethene	10	1
toxaphene		
trichlorobenzene	0.1 (1,2,4-TCB)	
trichloroethylene	10	1
trichloromethane	10	1
xylene	10 (each isomer)	10
Fourth priority		
aldrin	0.01	
chlordecone		
dieldrin	0.01	
DDT	0.002	0.1
endrin	0.005	
heptachlor	0.004 (+ epoxide)	
hexabromobiphenyl		
mirex		
short chain chlor. paraffins		

Estonia	Drinking water (µg/l)
First priority	
benzo(b)fluoranthene	
benzo(k)fluoranthene	
benzo(ghi)perylene	
benzo(a)pyrene	
fluoranthene	
hexachlorobenzene	
indeno(1,2,3-cd)pyrene	
TCDD	
PAHs (total)	0.2
Second priority	
PCBs	0.2
pentachlorophenol	
lindane	
phenols (total)	0.5
pesticides (individual)	0.1
pesticides (total)	0.5
Third priority	
chlordane	
endosulfan	
fenthion	
nitrofen	
tetrachloroethene	
toxaphene	
trichlorobenzene	
trichloroethylene	
trichloromethane	200
xylene	
Fourth priority	
aldrin	
chlordecone	
dieldrin	
DDT	
endrin	
heptachlor	
hexabromobiphenyl	
mirex	
short chain chlor. paraffins	

Germany	Surface water general (µg/l)	Surface water aquatic life (mg/kg)	Sediment (mg/kg)	Fish (mg/kg)	Drinking water (µg/l)
First priority					
benzo(b)fluoranthene					
benzo(k)fluoranthene					
benzo(ghi)perylene					
benzo(a)pyrene			0.3/1.0		
fluoranthene					
hexachlorobenzene	0.01	0.001	0.040		0.1
indeno(1,2,3-cd)pyrene					
TCDD					
PAH(16)			3/10		
Second priority					
PCB (6)			0.05/0.1		
pentachlorophenol					0.1
lindane					0.1
Third priority					
chlordane					0.1
endosulfan					0.1
fenthion					0.1
nitrofen					0.1
tetrachloroethene		40			1
toxaphene					
1,2,3-trichlorobenzene		8			1
1,2,4-trichlorobenzene		4			1
1,3,5-trichlorobenzene		20			0.1
trichloroethylene		20			1
trichloromethane		0.8			1
xylene					
Fourth priority					
aldrin				0.2 (sum)	0.1
chlordecone					0.1
dieldrin					0.1
DDT				5.0 (sum)	0.1
endrin					0.1
heptachlor					0.1
hexabromobiphenyl					
mirex					
short chain chlor. paraffins					

Romania	Surface water fresh (l) (µg/l)	Drinking water (µg/l)
First priority		
benzo(b)fluoranthene		
benzo(k)fluoranthene		
benzo(ghi)perylene		
benzo(a)pyrene		
fluoranthene		
hexachlorobenzene		
indeno(1,2,3-cd)pyrene		
TCDD		
sum PAH	0.2	0.001
Second priority		
PCBs		
pentachlorophenol		
lindane		
chlorophenols		
Third priority		
chlordane		
endosulfan		
fenthion		
nitrofen		
tetrachloroethene		
toxaphene		
trichlorobenzene		
trichloroethylene		
trichloromethane		
xylene		
Fourth priority		
aldrin		
chlordecone		
dieldrin		
DDT		
endrin		
heptachlor		
hexabromobiphenyl		
mirex		
short chain chlor. paraffins		

Slovak republic	Surface water water sources (µg/l)	Surface water other sources (µg/l)	Drinking water (µg/l)
First priority			
benzo(b)fluoranthene			
benzo(k)fluoranthene			
benzo(ghi)perylene			
benzo(a)pyrene	0.01	0.05	0.01
fluoranthene			
hexachlorobenzene			
indeno(1,2,3-cd)pyrene			
TCDD			
sum PAH			
Second priority			
PCBs		0.25	
pentachlorophenol			
lindane			
chlorophenols			
Third priority			
chlordane			
endosulfan			
fenthion			
nitrofen			
tetrachloroethene			
toxaphene			
trichlorobenzene			
trichloroethylene			
trichloromethane			
xylene			
Fourth priority			
aldrin			
chlordecone			
dieldrin			
DDT			
endrin			
heptachlor			
hexabromobiphenyl			
mirex			
short chain chlor. paraffins			

Slovenia	Surface water (I) (µg/l)	Surface water (II) (µg/l)
First priority		
benzo(b)fluoranthene		
benzo(k)fluoranthene		
benzo(ghi)perylene		
benzo(a)pyrene		
fluoranthene		
hexachlorobenzene		
indeno(1,2,3-cd)pyrene		
TCDD		
sum PAH	0.2	
Second priority		
PCBs		
pentachlorophenol	50	300
lindane	50	
Third priority		
chlordane		
endosulfan		
fenthion		
nitrofen		
tetrachloroethene		
toxaphene	5	
trichlorobenzene		
trichloroethylene	500	10000
trichloromethane		
xylene		
Fourth priority		
aldrin		
chlordecone		
dieldrin		
DDT		
endrin	1	10
heptachlor		
hexabromobiphenyl		
mirex		
short chain chlor. paraffins		

The Netherlands	Surface water (µg/l)	Sediment (mg/kg)	Fish (mg/kg)	Drinking water (µg/l)
First priority				
benzo(b)fluoranthene				0.05
benzo(k)fluoranthene	0.04	2.4		0.05
benzo(ghi)perylene	0.03	7.5		0.05
benzo(a)pyrene	0.05	0.26		0.05
fluoranthene	0.3	2.6		0.05
hexachlorobenzene	0.0021	0.028		
indeno(1,2,3-cd)pyrene	0.04	5.9		0.05
TCDD				
Sum PAH (16 EPA)				0.2
Second priority				
PCBs		0.02	0.04 – 0.12	
pentachlorophenol	3.5	0.31		
lindane	0.77	0.19		0.1
Third priority				
chlordane	0.0015	0.0024		0.1
endosulfan	0.0004	0.000026		0.1
fenthion	0.0031	0.00035		0.1
nitrofen				0.1
tetrachloroethene	330	4		0.1
toxaphene				0.1
trichlorobenzene	67	6.7		
trichloroethylene	2400	13		
trichloromethane	590	1.9		0.005
xylene	380	14		
Fourth priority				
aldrin	0.018	0.12		0.1
chlordecone				0.1
dieldrin	0.018	0.67		0.1
DDT	0.00044	0.0094		0.1
endrin	0.003	0.0029		0.1
heptachlor	0.00046	0.00065		0.1
hexabromobiphenyl				
mirex				0.1
short chain chlor. paraffins				

PCBs in fish depend on specific PCB congener and type of fish. Data are thresholds for consumption of fish other than eel. Data for eel are 5 times higher, data for fish liver are 15 times higher. Sum of pesticides in drinking water may not exceed 0.5 µg/l.

United Kingdom	Surface water fresh (µg/l)	Surface water marine (µg/l)
First priority		
benzo(b)fluoranthene		
benzo(k)fluoranthene		
benzo(ghi)perylene		
benzo(a)pyrene		
fluoranthene		
hexachlorobenzene		
indeno(1,2,3-cd)pyrene		
TCDD		
Second priority		
PCBs		
pentachlorophenol		
lindane		
Third priority		
chlordane		
endosulfan	0.003	0.003
fenthion		
nitrofen		
tetrachloroethene	10	
toxaphene		
trichlorobenzene	1	
trichloroethylene		
trichloromethane		
xylene		
Fourth priority		
aldrin		
chlordecone		
dieldrin		
DDT		
endrin		
heptachlor		
hexabromobiphenyl		
mirex		
short chain chlor. paraffins		

United States	Surface water fresh acute (µg/l)	Surface water fresh chronic (µg/l)	Surface water marine acute (µg/l)	Surface water marine chronic (µg/l)	Drinking water (µg/l)
First priority					
benzo(b)fluoranthene					(y)
benzo(k)fluoranthene					(y)
benzo(ghi)perylene					(y)
benzo(a)pyrene					(y)
fluoranthene	3980		40	16	(y)
hexachlorobenzene	6.0	3.68			(y)
indeno(1,2,3-cd)pyrene					
TCDD					
Second priority					
PCBs	2.0	0.014	10	0.03	0.5 (y)
pentachlorophenol	20	13	13	7.9	1 (n)
lindane	2.0	0.08	0.16		0.2 (y)
Third priority					
chlordane	2.4	0.0043	0.09	0.004	2 (y)
endosulfan	0.22	0.056	0.034	0.0087	(n)
fenthion					
nitrofen					
tetrachloroethene	5280	840	10200	450	5 (y)
toxaphene					
trichlorobenzene					
trichloroethylene	45000	21900	2000		5 (y)
trichloromethane	28900	1240			(y)
xylene					10000 (n)
Fourth priority					
aldrin	3.0		1.3		(y)
chlordecone					
dieldrin	2.5	0.0019	0.71	0.0019	(y)
DDT	1.1	0.001	0.13	0.001	(y)
endrin	0.18	0.0023	0.037	0.0023	(n)
heptachlor	0.52	0.0038	0.053	0.0036	0.4 (y)
hexabromobiphenyl					
mirex					
short chain chlor. paraffins					

Pentachlorophenol (drinking water): proposed criterion

Between brackets for drinking water: carcinogen y/n

WHO	Drinking water (µg/l)
First priority	
benzo(b)fluoranthene	insufficient data
benzo(k)fluoranthene	insufficient data
benzo(ghi)perylene	insufficient data
benzo(a)pyrene	0.7
fluoranthene	
hexachlorobenzene	1
indeno(1,2,3-cd)pyrene	insufficient data
TCDD	
Second priority	
PCBs	
pentachlorophenol	9 (P)
lindane	2
Third priority	
chlordane	0.2
endosulfan	
fenthion	
nitrofen	
tetrachloroethene	40
toxaphene	
trichlorobenzene	20 (total) 5-50 (odour, taste)
trichloroethylene	70 (P)
trichloromethane	200
xylene	500
Fourth priority	
aldrin	0.03
chlordecone	
dieldrin	0.03
DDT	2
endrin	
heptachlor	0.03 (and epoxide)
hexabromobiphenyl	
mirex	
short chain chlor. paraffins	

Annex 2 List of symbols used in the methods to assess the risk of POPs in aquatic ecosystems.

Table A2.1 General notation of symbols in the models.

Entity		Process		Compartment/Phase	
F =	flux ($m.yr^{-1}$)	bur =	burial	arm =	atmopshere
ct =	content ($g.kg^{-1}$)	deg =	degradation	doc =	dissolved organic carbon
[ ] =	concentration ($g.m^{-3}$)	dif =	diffusion	pw =	pore water
fr =	fraction ($kg.kg^{-1}$)	inf =	infiltration	sed =	sediment
A =	area (m^2)	lo =	lateral outflow	sus =	suspension
		res =	resuspension	unc =	uncomplexed
		sed =	sedimentation	w =	water
		sp =	seepage		
		vol =	volatilisation		

Table A2.2 Explanation of symbols in the risk assessment models.

Symbol	Explanation	Unit
A_c	the surface area of the catchment	(m^2)
A_l	the surface area of the lake	(m^2)
$ctX_{crit,sed}$	the critical adsorbed content of X in the sediment	($g.kg^{-1}$)
$ctX_{doc,pw}$	the content of X on (complexed with) dissolved organic carbon in the pore water of the sediment	($g.kg^{-1}$)
$ctX_{doc,w}$	the content of X on (complexed with) dissolved organic carbon in the water	($g.kg^{-1}$)
ctX_{sed}	the adsorbed content of X in the sediment	($g.kg^{-1}$)
ctX_{sus}	the adsorbed content of X in suspended particles	($g.kg^{-1}$)
D_{eff}	the effective diffusivity in the sediment	($m^2.yr^{-1}$)
$D_{mol,w}$	the molecular diffusivity in the water	($m^2.yr^{-1}$)
DOC_{pw}	the concentration of dissolved organic carbon in the pore water	($kg.m^{-3}$)
DOC_w	the concentration of dissolved organic carbon in the water	($kg.m^{-3}$)
$fr_{oc,sed}$	the fraction organic carbon in the sediment	($kg.kg^{-1}$)
$fr_{oc,sus}$	the fraction organic carbon in suspended particles	($kg.kg^{-1}$)
F_{netsed}	the net sedimentation flux of suspended particles	($m.yr^{-1}$)
F_{res}	the sedimentation flux of sediment particles	($m.yr^{-1}$)
F_{sed}	the sedimentation flux of suspended particles	($m.yr^{-1}$)
F_{sp}	the flux of water seeping through the sediment	($m.yr^{-1}$)
Q_l	the mass flow of water through the lake	($m^3.yr^{-1}$)
k_{atm}	the mass transfer coefficient in the air at the air-water interface	($m.yr^{-1}$)
kdeg	the overall rate constant for degradation of X in the catchment	(yr^{-1})
$k_{deg,sed}$	the overall rate constant for degradation of X in the sediment	(yr^{-1})
$k_{deg,w}$	the overall rate constant for degradation of X in the water	(yr^{-1})
k_l	the mass transfer coefficient between water and air	($m.yr^{-1}$)
k_w	the mass transfer coefficient in the water at the air-water interface	($m.yr^{-1}$)
K_k	Henry's law constant of X	(-)
K_{oc}	the adsorption coefficient of X to organic carbon	($m^3.kg^{-1}$)

Symbol	Explanation	Unit
$K_{p,doc}$	the adsorption coefficient of X to dissolved organic carbon	($m^3.kg^{-1}$)
$K_{p,sed}$	the adsorption coefficient of X to the sediment	($m^3.kg^{-1}$)
$K_{p,sus}$	the adsorption coefficient of X to suspended particles	($m^3.kg^{-1}$)
p	the porosity (volumetric water content) of the sediment	($m^3.m^{-3}$)
$R_{doc,pw}$	the ratio between total concentration in the sediment and adsorbed concentration on DOC in the pore water of the sediment	($kg.m^{-3}$)
$R_{doc,w}$	the ratio between total concentration in the water and adsorbed concentration on DOC	($kg.m^{-3}$)
R_{in}	the ratio between the total load of compound X on the lake and the total concentration of compound X in the water compartment	($m.yr^{-1}$)
R_{sed}	the ratio between total concentration in the sediment and adsorbed concentration in the sediment	($kg.m^{-3}$)
R_{sus}	the ratio between total concentration in the water and adsorbed concentration on suspended particles	($kg.m^{-3}$)
$R_{tot,w}$	the ratio between the total concentration in the sediment and the total concentration in the water	($m^3.m^{-3}$)
$R_{unc,pw}$	the ratio between total concentration in the sediment and uncomplexed dissolved concentration in the pore water of the sediment	(-)
$R_{unc,w}$	the ratio between total concentration and uncomplexed dissolved concentration in the water	(-)
sus	the concentration of suspended particles in the water	($kg.m^{-3}$)
t	the mean residence time in the catchment area between entry in the catchment area and arrival at the lake	(yr)
x_{doc}	a factor to account for the less efficient adsorption to DOC with respect to particulate organic carbon	(-)
$X_{bd,sed}$	the loss of X from the sediment by biodegradation	($g.m^{-2}.yr^{-1}$)
$X_{bd,w}$	the loss of X from the water by biodegradation	($g.m^{-2}.yr^{-1}$)
X_{bur}	the loss of X as a result of burial of sediment	($g.m^{-2}.yr^{-1}$)
$X_{deg,sed}$	the total loss of X from the sediment by degradation	($g.m^{-2}.yr^{-1}$)
$X_{deg,w}$	the total loss of X from the water by degradation	($g.m^{-2}.yr^{-1}$)
X_{dd}	the direct atmospheric deposition flux of compound X on the lake	($g.m^{-2}.yr^{-1}$)
X_{dif}	the amount of X that is transported from the water to the sediment or vice versa by diffusion	($g.m^{-2}.yr^{-1}$)
X_{dl}	the direct load of X on the lake	($g.m^{-2}.yr^{-1}$)
X_{dol}	the direct other loads of X on the lake	($g.m^{-2}.yr^{-1}$)
$X_{hy,sed}$	the loss of X from the sediment by hydrolysis	($g.m^{-2}.yr^{-1}$)
$X_{hy,w}$	the loss of X from the water by hydrolysis	($g.m^{-2}.yr^{-1}$)
X_{id}	the indirect load of X on the lake, coming from atmospheric deposition flux on the catchment	($g.m^{-2}.yr^{-1}$)
X_{il}	the indirect load of X on the lake	($g.m^{-2}.yr^{-1}$)
X_{iol}	the indirect load of X on the lake, coming from other loads on the catchment	($g.m^{-2}.yr^{-1}$)
X_{inf}	the amount of X that is transported from the water to the sediment by infiltrating water	($g.m^{-2}.yr^{-1}$)
X_{lo}	the loss of X by lateral outflow of water	($g.m^{-2}.yr^{-1}$)
$X_{ml,l}$	the effect-based maximum load of X for the lake	($g.m^{-2}.yr^{-1}$)
$X_{ml,c}$	the effect-based maximum load of X for the catchment	($g.m^{-2}.yr^{-1}$)
$X_{ph,w}$	the loss of X from the water by photolysis	($g.m^{-2}.yr^{-1}$)
X_{res}	the amount of X that is transported from the sediment to the water by resuspension	($g.m^{-2}.yr^{-1}$)
X_{sed}	the amount of X that is transported from the water to the sediment by sedimentation	($g.m^{-2}.yr^{-1}$)
X_{sp}	the loss of X by seepage	($g.m^{-2}.yr^{-1}$)
X_{tl}	the total load of X on the lake	($g.m^{-2}.yr^{-1}$)

Symbol	Explanation	Unit
X_{vol}	the loss of X by volatilisation	($g.m^{-2}.yr^{-1}$)
$[X]_{atm}$	the concentration of X in the atmosphere	($g.m^{-3}$)
$[X]_{crit,tot,w}$	the critical total concentration of X in the water	($g.m^{-3}$)
$[X]_{crit,unc,w}$	the critical uncomplexed dissolved concentration of X in the water	($g.m^{-3}$)
$[X]_{tot,pw}$	the total concentration of X in the pore water	($g.m^{-3}$)
$[X]_{tot,sed}$	the total concentration of X in the sediment	($g.m^{-3}$)
$[X]_{tot,w}$	the total concentration of X in the water	($g.m^{-3}$)
$[X]_{unc,pw}$	the uncomplexed dissolved concentration of X in the pore water of the sediment	($g.m^{-3}$)
$[X]_{unc,w}$	the uncomplexed dissolved concentration of X in the water	($g.m^{-3}$)
z_{dif}	the diffusion path length at the water-sediment interface	(m)
z_{sed}	the depth of the sediment compartment	(m)
z_w	the depth of the water compartment	(m)
ρ_{sed}	the dry bulk density of the sediment	($kg.m^{-3}$)