

### 5.5 Critical Loads of cadmium, lead and mercury

#### 5.5.1 General methodological aspects of mapping critical loads of heavy metals

##### 5.5.1.1 Calculation of different types of critical loads

The method to calculate critical loads of heavy metals is based on the balance of all relevant metal fluxes in and out of a considered ecosystem in a steady state situation. In order to keep the approach compatible with the simple mass balance approach used for nitrogen and acidity, the internal metal cycling within an ecosystem is ignored, such that calculations can be kept as simple as possible. In consequence the critical load of a metal can be calculated from the sum of tolerable outputs from the considered system in terms of net metal uptake and metal leaching.

The assumption of steady state signifies that the concentration in the system does not change in time because the amount of heavy metal entering the system is equal to the amount that leaves the system. The validity of this assumption depends on the magnitude of the time scales of the various input and output processes. If e.g. a metal sorbs very strongly to the soil, it may take a long time (up to hundreds of years), before a steady state is reached. This has to be kept in mind when comparing a present load with the critical load (De Vries and Bakker 1998). Critical loads of cadmium (*Cd*), lead (*Pb*) and mercury (*Hg*) can be calculated in dependence on the receptors and the metal of concern. Critical limits of these heavy metals addressing either ecotoxicological ecosystem effects or human health effects are derived with specific approaches. Critical loads on the basis of such limits should be calculated separately for aquatic and terrestrial ecosystems. In consequence four types of critical loads can be derived for each metal, an overview is provided in Table 5.17, which is however not a complete review of

possible effects of these metals.

Indicators of effects on ecosystems listed in Table 5.17 are mainly ecotoxicological effects. Secondary poisoning through the food chain has also been studied (De Vries et al. 2003). These effects give partly more stringent critical limits, however their modelling includes more uncertainties and is therefore not considered in this manual.

Critical loads for terrestrial ecosystems addressing human health effects can be calculated, either in view of not violating food quality criteria in crops or in view of ground water protection (keeping quality criteria for drinking water of WHO 2004). An appropriate indicator for critical load calculations addressing human health effects via food intake is the *Cd* content in wheat. Keeping a conservative food quality criterion for wheat, as described in Section 5.5.2.2.1, protects at the same time against effects on human health via other food and fodder crops (including also the quality of animal products, since the pathway of *Cd* to wheat leads to the lowest critical *Cd* content in soils according to De Vries et al. (2003)). Such critical load calculations are in principle also possible for lead, and for other food and fodder crops, if the soil-plant transfer can be described with sufficient accuracy and can be done in addition on a voluntary basis.

Among terrestrial ecosystems, critical loads of *Cd* and *Pb* are to be calculated from the viewpoint of ecotoxicology for areas covered by non-agricultural land (forests, semi-natural vegetation) or agricultural land (arable land and grassland). Organic forest (top)soils are considered as the only critical receptor with respect to atmospheric *Hg* pollution, based on knowledge on effects on microbial processes and invertebrates (Meili et al. 2003a). The critical exposure of terrestrial ecosystems to atmospheric *Hg* pollution can be calculated in much the same way as for *Pb* and *Cd* by a simple mass balance, as discussed in Section 5.5.2.1.

## 5 Mapping Critical Loads

**Table 5.17:** Four types of critical loads of *Pb*, *Cd*, *Hg*, related receptors and indicators

Receptor ecosystem	Critical loads related to	Metals of concern	Land cover types to be considered	Indicator addressed by the critical limit
1) Terrestrial <sup>*)</sup>	a) Human health effects	Cd, <i>Pb</i> , <i>Hg</i>  <i>Cd, Pb, Hg</i>  Cd, Pb, Hg	Arable land  <i>Grassland</i>  Arable land, grassland, non-agricultural land	Metal content in food/fodder crops  <i>Metal content in grass, animal products (cow, sheep)</i>  Total metal concentration in soil water below the rooting zone (aiming at ground water protection )
	b) Ecosystem functioning	Pb, Cd, Hg	Non-agricultural land, arable land, grassland,  Forests only	Free metal ion concentration in soil solution in view of effects on soil micro-organisms, plants and invertebrates  Total metal concentration in humus layer in view of effects on soil micro-organisms and invertebrates
2) Aquatic	a) Human health effects	Hg	Freshwaters	Metal concentration in fish
	b) Ecosystem functioning	Pb, Cd, Hg	Freshwaters	Total metal concentration in freshwaters in view of effects on algae, crustacea, worms, fish, top predators

<sup>\*)</sup> In italics: these calculations can be done in addition on a voluntary basis. To perform such calculations, more information on the derivation of critical limits based on critical metal contents in food/fodder crops and in animal products is given in Annex 2 and 3, respectively, of the background document (De Vries et al. 2005).

For aquatic ecosystems the critical limits of *Pb* and *Cd* are related to ecotoxicological effects, while human health effects by this pathway are less relevant and therefore not considered here. Critical limits of *Hg* refer to both human health effects (*Hg* concentration in fish and other animals that serve as a food source to humans) and ecotoxicological effects, since microbiota and higher wildlife itself may also be affected.

Although it might be useful to calculate and map each of the different types of critical loads and the critical *Hg* level in precipitation separately for comparison purposes, the aim is ultimately to provide maps for at most four critical loads per metal (or *Hg* level, respectively) related to:

- Ecotoxicological effects for all terrestrial ecosystems.

- Human health effects for all terrestrial ecosystems.
- Ecotoxicological effects for all aquatic ecosystems.
- Human health effects for all aquatic ecosystems.

If different indicators within each category (map) have been considered (e.g. *Cd* in wheat and *Cd* in soil drainage water in view of ground water protection for human health), the final map should indicate the minimum critical *Cd* load for both effects to human health. The reason for providing different critical loads for different types of ecosystems is because the critical load for terrestrial ecosystems does not automatically protect aquatic ecosystems, receiving much or most of their metal load by drainage from the surrounding soils, and vice versa.

A critical load indicates only the sensitivity of an ecosystem against the anthropogenic input of the metal of interest. It implies a potential risk at sites where the critical load is exceeded. In agricultural ecosystems, the exceedance of critical loads of heavy metals is not only determined by atmospheric inputs (being generally the only source in non-agricultural ecosystems), but by total inputs, including fertilizer and animal manure inputs.

### 5.5.1.2 Limitations in sites that allow critical load calculations

Critical load calculations can not be carried out for sites with:

- Negative water balances, since there is no leaching but a seepage influx of water, leading to accumulation of salts and very high *pH*; such regions do, however, hardly occur in Europe.
- Soils with reducing conditions (e.g. wetlands), because the transfer functions do not apply for such soils. In the topsoil, to which the critical load calculations apply, such situations do, however, hardly occur apart from water logged soils where the simplified critical load calculation can not be applied anyhow because of a deviating hydrology.

Weathering inputs of metals are neglected due to i) low relevance of such inputs and ii) high uncertainties of respective calculation methods. It is, however, recommended to use estimates of weathering rate to identify sites with a high geogenic metal input, where natural weathering may already exceed the critical load. This should be considered, when critical limits and loads exceedances are to be interpreted. For methods to calculate weathering rates, see De Vries and Bakker (1998) and Hettelingh et al. (2002). More information on how sites with high geogenic contents of metals can be identified are described in Farret et al. (2003). The most important information is summarised in Annex 6 of the background document (De Vries et al. 2004b).

### 5.5.1.3 Definitions and symbols/abbreviations used in critical load calculations

General definitions of critical loads, critical levels and exceedances, and others can be found in the related chapters of the Modelling and Mapping Manual. The following definitions refer specifically to the application in the context of critical loads of heavy metals.

#### Definitions

The receptor is a living element of the environment that is subject to an adverse effect. It can be a species of interest including human beings, or several species considered representative of a larger group (e.g. plants, soil invertebrates, fish, algae, etc), or the whole ecosystem (typically the subject of interest in the critical load approach).

The critical limit is a concentration threshold within the ecosystem, based on adverse effects, i.e. it is a short expression of “effect-based critical limit”. Below this critical limit significant harmful effects on human health or specified sensitive elements of the environment do not occur, according to present knowledge. To avoid confusion, limits that are not based on effects should not be called “critical limits”.

The critical load is the highest total metal input rate (deposition, fertilisers, other anthropogenic sources) below which harmful effects on human health as well as on ecosystem structure and function will not occur at the site of interest in a long-term perspective, according to present knowledge. The critical load is derived from the critical limit through a biogeochemical flux model, assuming steady-state for the fluxes as well as chemical equilibrium (which is a theoretical situation in an undetermined future, consistent with concepts of sustainability). For this purpose the critical limit has to be transformed to a critical total concentration of the metal in the output fluxes by water (leaching from the soil or outflow from an aquatic ecosystem).

## 5 Mapping Critical Loads

An overview of used symbols and abbreviations is given below (Table 5.18).

### Some general abbreviations:

$M$	= a flux of a metal $M$
$[M]$	= a content (in soil, plants, other biota) or a concentration (in a liquid) of a metal $M$
$[M]_{...(\text{crit})}$	= a critical content (in soil, plants, other biota) or a critical concen-

$f$	tration (in a liquid) of a metal $M$ , not explicitly explained in table 5.18 for all the individual contents or concentrations
$c$	= a fraction
$sdw$	= a factor for conversion of units, not explained in the table
$sw$	= in soil drainage water
	= in surface water

**Table 5.18:** Symbols and abbreviations used in the calculation of critical loads of heavy metals

Symbols	Short explanation	Basic units
CL (M)	critical load of a metal (M)	[g ha <sup>-1</sup> a <sup>-1</sup> ]
$M_u$	metal net uptake in harvestable parts of plants (under critical load conditions)	[g ha <sup>-1</sup> a <sup>-1</sup> ]
$M_w$	weathering rate of a metal	[g ha <sup>-1</sup> a <sup>-1</sup> ]
$M_{le(\text{crit})}$	critical leaching flux of a metal with drainage water	[g ha <sup>-1</sup> a <sup>-1</sup> ]
$M_{ret(\text{crit})}$	net retention of a metal in the aquatic system at critical load	[g ha <sup>-1</sup> a <sup>-1</sup> ]
$M_{lo(\text{crit})}$	critical lateral outflow of a metal from the aquatic system	[g ha <sup>-1</sup> a <sup>-1</sup> ]
$Y_{ha}$	yield of harvestable biomass	[kg dw ha <sup>-1</sup> a <sup>-1</sup> ]
$z_b$	depth of the upper, biologically active soil layer (topsoil)	[m]
$z$	depth of the rooting zone	[m]
$Q_{le,zb}$	leaching flux of water from the topsoil	[m a <sup>-1</sup> ]
$Q_{le,z}$	leaching flux of water from the rooting zone	[m a <sup>-1</sup> ]
$Q_{lo}$	lateral outflow flux of water from the aquatic system	[m a <sup>-1</sup> ]
$P / E_i / E_s / E_t$	symbols for water fluxes (water balance equation): Precipitation/ interception evaporation / soil evaporation / (plant) transpiration, resp.	[m a <sup>-1</sup> ]
$f_{Mu,zb}$	fraction of metal net uptake within the topsoil	[ $\cdot$ ]
$f_{Mu,z}$	fraction of metal net uptake within the entire rooting zone	[ $\cdot$ ]
$f_{Et,zb}$	fraction of water uptake by plants within the topsoil	[ $\cdot$ ]
$f_f$	fractionation or transfer factor describing the Hg contamination of organic matter in solution relative to that in solids	[ $\cdot$ ]
$A_l$	lake area	[ha]
$A_c$	catchment area	[ha]
$TF_{Hg\text{Site}}$	site-specific transfer function linking fish Hg to atmospheric Hg	[l kg <sup>-1</sup> fw]
$TF_{Hg\text{Run}}$	transfer function referring to the transfer of atmospheric Hg to fish flesh via runoff in a reference watershed at steady state	[l kg <sup>-1</sup> fw]
$TF_{Hg\text{Bio}}$	organism-specific transfer function addressing Hg partitioning within food webs	[ $\cdot$ ]
$[M]_{ha}$	metal content in harvestable biomass	[mg kg <sup>-1</sup> dw]
$[M]_{re}$	reactive content of a metal in soil	[mg kg <sup>-1</sup> ]
$[M]_{AR}, [M]_{HF}, [M]_{EDTA}, [M]_{HNO_3}$	concentration of a metal in soil, extracted with Aqua Regia, HF, EDTA, HNO <sub>3</sub> respectively.	[mg kg <sup>-1</sup> ]
$[M]_{dis,sw}$ or $[M]_{dis,sw}$	total dissolved metal concentration in soil drainage water, or in surface water, respectively	[mg m <sup>-3</sup> ]
$[M]_{tot,sw}$ or $[M]_{tot,sw}$	total metal concentration in soil drainage water, or in surface water, including both dissolved metal and metal in suspended particles	[mg m <sup>-3</sup> ]

$[M]_{\text{free, sdw}}$ or $[M]_{\text{free, sw}}$	concentration of free metal ion in soil drainage water, or in surface water, respectively	$\text{mol l}^{-1}$
$[M]_{\text{DIC, sdw}}$	concentration of metal bound to dissolved inorganic complexes in soil drainage water	$\text{mg m}^{-3}$
$[M]_{\text{DOM, sdw}}$	concentration of metal bound to dissolved organic matter in soil drainage water	$\text{mg m}^{-3}$
$[M]_{\text{SPM, sdw}}$ or $[M]_{\text{SPM, sw}}$	concentration of metal bound to suspended particulate matter in soil drainage water, or in surface water, respectively	$\text{mg kg}^{-1}$
$[\text{Hg}]_{\text{OM}}$	concentration of Hg, normalised for $[\text{OM}]_s$	$\text{mg} (\text{kg OM})^{-1}$
$[\text{Hg}]_{\text{Pike}}$	Hg concentration in the flesh of 1-kg pike	$\text{mg kg}^{-1} \text{ fw}$
$[\text{Hg}]_{\text{Bio}}$	Hg concentration in biota, e.g. fish flesh	$\text{mg kg}^{-1} \text{ fw}$
$[\text{Hg}]_{\text{Prec}}$	Hg concentration in precipitation	$\text{ng l}^{-1}$
$[\text{clay}]$	clay content of the soil	$[(\text{kg clay}) \text{ kg}^{-1}]$ or [%]
$[\text{OM}]_s$	organic matter content of the soil	$[(\text{kg OM}) \text{ kg}^{-1}]$ or [%]
$[\text{DOM}]_{\text{sdw}}$ or $[\text{DOC}]_{\text{sdw}}$	concentration of dissolved organic matter, or dissolved organic carbon, respectively, in soil drainage water	$\text{g m}^{-3}$ or $[\text{mg l}^{-1}]$
$[\text{TOC}]_{\text{sw}}$	concentration of total organic carbon in surface water	$\text{g m}^{-3}$ or $[\text{mg l}^{-1}]$
$[\text{TP}]_{\text{sw}}$	concentration of total phosphorus in surface water	$\mu\text{g l}^{-1}$ or $[\text{mg l}^{-1}]$
$[\text{SPM}]_{\text{sdw}}$ or $[\text{SPM}]_{\text{sw}}$	concentration of suspended particulate matter in soil drainage water, or in surface water, respectively	$\text{kg m}^{-3}$
$\text{pH}_{\text{sdw}}$ or $\text{pH}_{\text{sw}}$	pH value in soil drainage water, or in surface water	[-]

### 5.5.1.4 Stand-still approach versus calculation of critical limit exceedance

The harmonised methodological basis for a first preliminary calculation and mapping of critical loads of *Cd* and *Pb* related to ecotoxicological effects (Hettelingh et al. 2002), was based on a guidance document (De Vries et al. 2002). In this document a stand-still approach, which aims at avoiding any (further) accumulation of heavy metals in the soil, was also included as an alternative to the effect-based approach. This method is, however, not included in this manual since it implies the continued addition of metals on historically polluted soils with high leaching rates. The current leaching may then already imply significant effects, both on terrestrial as well as aquatic ecosystems receiving the drainage water from the surrounding soils, and is thus not per se acceptable in the long term. Furthermore, it does lead to critical load exceedance at soils which strongly adsorb heavy metals, whereas the effect does occur through the soil solution.

Instead, it is suggested to calculate critical concentrations of metals in the soil, the soil drainage water or the surface water based on the critical limits and compare these to the present soil or water metal concentrations to assess the critical limit exceedance in the present situation. This implies that one has to map the present metal concentrations in the country (expressed as total or reactive soil contents, total dissolved concentrations or even free ion concentrations). Such a comparison can be seen as an intermediate step for dynamic models for heavy metals. If the present soil metal content exceeds the critical concentration (limit), the metal input has to be less than the critical load to reach the critical concentration at a defined time period. In the reverse case, the metal input can be larger than the critical load for a defined time period not exceeding during that period the critical concentration. However, only keeping the critical load will not lead to exceedance of the critical limit in the long run. More information on how to calculate the critical concentration is given in the background document.

### 5.5.2 Terrestrial ecosystems

#### 5.5.2.1 Simple steady-state mass balance model and related input data

##### 5.5.2.1.1 Steady-state mass balance model

The method to calculate critical loads of heavy metals for terrestrial ecosystems is focusing in particular on the upper soil layer. The critical load of a metal can be calculated as the sum of tolerable outputs from this considered soil layer by harvest and leaching minus the natural inputs by weathering release (De Vries and Bakker, 1998). Because weathering causes only a minor flux of metals in topsoils, while uncertainties of such calculations are very high, the model was further simplified by assuming that weathering is negligible within the topsoil outside ore-rich areas. As mentioned in the introduction of this chapter, the calculation of weathering rates is recommended to identify areas, where the natural input exceeds tolerable outputs; and such sites can be excluded from the database, subject to decision by the National Focal Centres.

The described approach implies that the critical load equals the net uptake by forest growth or agricultural products plus an acceptable metal leaching rate:

(5.88)

$$CL(M) = M_u + M_{le(crit)}$$

where:

$CL(M)$  = critical load of a heavy metal

$M$  ( $g\ ha^{-1}\ a^{-1}$ )

$M_u$  = metal net uptake in harvestable parts of plants under critical load conditions ( $g\ ha^{-1}\ a^{-1}$ )

$M_{le(crit)}$  = critical leaching flux of heavy metal  $M$  from the considered soil layer ( $g\ ha^{-1}\ a^{-1}$ ), whereby only the vertical drainage flux is considered

The notation has been related to the critical load equations for acidity and nutrient nitrogen:  $M$  stands for flux of a heavy metal and

can be substituted by the chemical symbol of the individual metal ( $Cd$ ,  $Pb$ ,  $Hg$ ) under consideration. The critical metal leaching  $M_{le(crit)}$  refers to the total vertical leaching rate, including dissolved, colloidal and particulate (metal) species in the drainage water. For a critical load, the critical metal leaching is based on a critical (toxic) metal concentration in soil or the (free ion or total) metal concentration in soil water.

In mass balance models for  $Hg$ , re-emission (volatilization) of deposited  $Hg$  occurs as an additional flux. This flux can, however, be ignored when calculating critical loads of  $Hg$ , because this re-emission is treated as part of the atmospheric net deposition in the modelling by EMEP MSC-E (Ryaboshapko et al. 1999, Ilyin et al. 2001). Therefore, in order to avoid double consideration in the calculation of critical load exceedances, it should be excluded from the critical loads model.

Appropriate and consistent calculation of critical loads for terrestrial ecosystems requires a consistent definition of the topsoil compartment and its boundaries. The depth can be variable. Relevant boundaries have been derived considering on one hand the expected probability of adverse impacts on the main target groups of organisms (plants, soil invertebrates, soil microbiota), or ground water quality, and on the other hand the occurrence and location of relevant metal fluxes within the soil profile:

-For  $Pb$  and  $Cd$  it is assumed that ecotoxicological effects as well as the main proportion of uptake by plants occur in (from) the organic layer ( $O$  horizon) and the humus rich (top)soil horizons ( $A_h$ ,  $A_p$ ). Therefore the depth of the biological active topsoil ( $z_b$ ) should be considered for arable land, grassland, and forests as far as the critical load calculations are addressing ecotoxicological effects, or the protection of food/fodder quality, respectively. For forest soils covered by an organic layer, the critical loads for both the organic layer, and the upper mineral horizon should be calculated separately. In these

cases the most sensitive of both layers should be presented in the critical loads map. For all terrestrial ecosystems the maximum depth of the topsoil ( $z_b$ ) to be considered is the lower boundary of the uppermost mineral horizon (in most soil classification systems called the A-horizon).

Default values of  $z_b$  are:

for forests: 0.1 m ( $O$  and/or  $A_h$  horizon)  
 grassland: 0.1 m ( $A_h$  horizon)  
 arable: 0.3 m ( $A_p$  horizon, plough layer)

-Regarding  $Hg$ , the critical receptor in terrestrial ecosystems is the organic topsoil (mor or humus layer) of forest soils ( $O$ -horizon excluding litter, which is sometimes divided into L, F and H horizons), where microbial processes are suspected to be affected. For calculating the critical load of  $Hg$  in forests, the topsoil is therefore defined as the humus layer, excluding underlying mineral soil layers.

Note, that for calculations of critical loads with respect to protection of groundwater quality the entire soil column has to be included. However, it is preliminarily not planned within the critical loads work to model the whole pathway of the metal flux with drainage water, considering the binding capacity of layers between rooting zone and upper groundwater. Therefore, for simplification the critical leaching of metals from the viewpoint of ground water protection is calculated by multiplying the drainage water flux below the rooting zone (soil depth =  $z$ ) with the critical limit for drinking water (see 5.5.2.2).

### 5.5.2.1.2 Heavy metal removal from the topsoil by net growth and harvest of plants

For critical load calculations, the removal of heavy metals refers to a future steady-state level where critical limits in the ecosystem compartments are just reached (critical loads conditions). The calculation of a critical removal of metals on the basis of a

critical concentration for soil solution is hardly practicable since for many metals there are no clear relationships between concentrations in soil solution (or even free metal ions) and the content of the metals in harvestable part of the plants. Reasons are amongst others the plant specific exclusion of metals from root uptake or accumulation in specific tissues (detoxification). An exception is the transfer of  $Cd$  from soil to wheat grains, used to calculate critical loads related to food quality criteria (see 5.5.2.2.1).

Therefore a simplified approach is proposed to describe the tolerable removal of heavy metals by biomass net uptake. The average yield (or growth increment) of harvestable biomass is multiplied with the heavy metal content in harvestable plant parts and with a factor to account for the fraction of metal uptake from the relevant soil layer relative to the uptake from the total rooting zone (eq. 5.89):

(5.89)

$$M_u = f_{Mu} \cdot Y_{ha} \cdot [M]_{ha}$$

where:

$M_u$  = metal net uptake in harvestable parts of plants under critical load conditions ( $g \text{ ha}^{-1} \text{ a}^{-1}$ ) (see eq. 5.88),

$f_{Mu}$  = fraction of metal net uptake within the considered soil depth ( $z_b$  or  $z$ ), accounting also for metal uptake due to deposition on vegetation surfaces (-); in calculations of critical loads to protect ground water,  $f_{Mu} = 1$ , otherwise  $f_{Mu}$  is a value between 0 and 1

$Y_{ha}$  = yield of harvestable biomass (dry weight) ( $kg \text{ ha}^{-1} \text{ a}^{-1}$ ),

$[M]_{ha}$  = metal content of the harvestable parts of the plants ( $g \text{ kg}^{-1} \text{ dw}$ ), including also metals deposited on vegetation surfaces (when the metal content is given in  $mg \text{ kg}^{-1} \text{ dw}$ , the value has to be divided by 1000).

As a default approximation, a root uptake factor ( $f_{Mu,zb}$ ) of 1 can be used for all ecosys-

tem types, assuming that most uptake of nutrients and pollutants occurs in the top soil. In forests values around 80 % have been reported for uptake from the humus layer alone (based on lead isotopes in Scots pine, Bindler et al. 2003). Thus, for calculations referring to the humus layer,  $f_{Mu,zb}$  may be 0.8, but, if the top of the underlying mineral soil is included in the calculations,  $f_{Mu,zb}$  is likely to approach 1, also in forests. If  $f_{Mu,zb}$  is 1, the uptake from the upper horizon is equal to that of the entire rooting depth (assumed to be limited to the depth where 90 % of the root biomass is distributed). This implies that there is no difference in the uptake calculation of critical loads related to ecotoxicological effects and in view of ground water protection. More detailed values of  $f_{Mu,zb}$  may be used, if information is available.

Data on yields for forests can in principle be obtained from the database of critical loads of acidity and nutrient nitrogen. Data on yields in agro-ecosystems are available from related statistics of the countries. The spatial pattern can be derived using information on land use as well as on soil quality and climate.

To get data on metal contents in harvestable biomass, studies from relatively unpolluted areas should be used. Median values (or averages) of metals contents in plants from such databases do in general not exceed quality criteria for food and fodder crops or phyto-toxic contents, respectively. Related fluxes can therefore be considered as tolerable. As far as appropriate national data are not available, the default values or ranges in Table 5.19 can be used for orientation, e.g. the average of a range.

If critical loads related to quality criteria of food or fodder are to be calculated, the critical concentrations in the harvestable plant parts should be multiplied with the yields (net crop removal), considering for arable land the coverage by the crops of interest, in order to calculate the tolerable output of metals by biomass harvest.

If contents are available for different harvested parts of the plants (e.g. stem and bark), a mass weighted mean should be used. Beware that only the net uptake is calculated. For instance, for agricultural land the amount of metals in stalks or the leaves of beets remaining on the field should not be considered. The removal of heavy metals in

**Table 5.19:** Ranges of mean values (averages, medians) of contents of Pb, Cd, and Hg in biomass for various species (harvestable parts)

Land use	Species	Metal content in harvestable plant parts, [M] <sub>ha</sub> [mg kg <sup>-1</sup> dw]		
		Pb	Cd	Hg
Grassland	mixed grassland species	1.0 - 3.0	0.05 - 0.25	0.01-0.1
Arable land	wheat (grains)	0.1	0.08	0.01
	other cereals (grains)	0.1 - 0.3	0.02 - 0.06	0.01
	potato	0.73	0.23	0.02
	sugar beet	1.0	0.25	0.02
	maize	3.8	0.2	0.04
Coniferous forest	spruce, pine, fir, douglas,			
	Central Europe	0.5- 10	0.1 - 0.5	0.01-0.05*
	Northern Europe	0.1/0.2**	0.02/0.04**	0.004/0.008**
Deciduous forest	oak, beech, birch, poplar	0.5 - 10	0.05 – 0.5	

\*) Hg in spruce stems  $\approx$  10-20% of needle content (Schuetze and Nagel 1998)

\*\*) Northern Sweden (Alriksson et al. 2002 and unpublished), for spruce stems without/with bark  
Other data sources: De Vries and Bakker (1998), Nagel et al. (2000), Jacobsen et al. (2002)

this case is the product of the yield of grains/beets and the mean contents in these parts of the plants. For forest ecosystems, only the net increment should be considered, but not the uptake into needles, leaves, etc., which also remain in the system.

In ecosystems with appreciable precipitation surplus or with a very limited growth, the removal of metals by harvest may often be very low compared to metal losses by leaching at critical load. In these cases the uptake calculation do not deserve high efforts. Instead, it is better to concentrate on sophisticated calculations for the critical leaching rate.

### 5.5.2.1.3 Critical leaching of heavy metals from the soil

The critical leaching flux of a heavy metal from the regarded soil layer can be calculated according to the equation:

(5.90)

$$M_{le(crit)} = c_{le} \cdot Q_{le} \cdot [M]_{tot, sdw(crit)}$$

where:

$M_{le(crit)}$  = critical leaching flux of heavy metal from the topsoil ( $g \text{ ha}^{-1} \text{ a}^{-1}$ ) (see eq. 5.88)

$Q_{le}$  = flux of drainage water leaching from the regarded soil layer defined as above ( $m \text{ a}^{-1}$ )

$[M]_{tot, sdw(crit)}$  = critical total concentration of heavy metal in the soil drainage water ( $mg \text{ m}^{-3}$ ) (derived from critical limits, see 5.5.2.2)

$c_{le}$  =  $10 \text{ g mg}^{-1} \text{ m}^2 \text{ ha}^{-1}$ , factor for appropriate conversion of flux units

### Flux of drainage water

In order to calculate critical loads in view of groundwater protection the data on precipitation surplus from the database on critical loads of acidity and nutrient nitrogen can be used. Deviating from this, the proportion of transpiration removing water from the upper

horizons ( $O$ , and/or  $A_h, A_p$ ) has to be accounted for by using a scaling (root uptake) factor when critical loads with respect to ecotoxicological effects or to food/fodder quality are addressed.

The drainage water flux leaching from the topsoil at the bottom of the topsoil ( $Q_{le, z_b}$ ) at steady state can be calculated according to:

(5.91a)

$$Q_{le, z_b} = P - E_i - E_s - f_{Et, z_b} \cdot E_t$$

where:

$P$  = precipitation ( $m \text{ a}^{-1}$ )

$E_i$  = interception evaporation ( $m \text{ a}^{-1}$ )

$E_s$  = actual soil evaporation within the topsoil defined as above ( $m \text{ a}^{-1}$ )

$E_t$  = actual plant transpiration ( $m \text{ a}^{-1}$ )

$f_{Et, z_b}$  = scaling or root uptake factor, fraction of water uptake within the topsoil (-)

This approach is based on the assumption that soil evaporation ( $E_s$ ) only takes place down to the depth  $z_b$ . Interception evaporation can be calculated as a function of the precipitation (De Vries et al. 1991). For sites without detailed water balance data, the annual mean water percolation  $Q_{le}$  can also be determined by the long-term mean annual temperature (mainly determining the potential evapotranspiration,  $E_{pot}$ ) and precipitation (mainly influencing the actual evapotranspiration,  $E_{act}$ ) according to:

(5.91b)

$$Q_{le, z_b} = P_m - f_{E, z_b} \cdot (P_m^{-2} + (e^{(0.063 \cdot T_m)} \cdot E_{m, pot})^{-2})^{-1/2}$$

where:

$P_m$  = annual mean precipitation ( $m \text{ a}^{-1}$ , data adjusted for common measurement bias)

$T_m$  = annual mean air temperature ( $^{\circ}C$ )

$E_{m, pot}$  = annual mean potential evapotranspiration in humid areas at  $T_m = 0^{\circ}C$ ;  $E_{m, pot} \approx 0.35 \text{ m a}^{-1}$  in forests, possibly less in other terrestrial ecosystems.

$f_{E,zb}$  = Fraction of total annual mean evapotranspiration above  $z_b$  (–);  
 $f_{E,zb} \approx 0.8$  for the organic top soil layer of forests.

For forested areas, this relationship is supported by data not only on river runoff but also on soil percolation (e.g. based on Michalzik et al. 2001), which together suggest that about 80% or more of the total evapotranspiration takes place above or within the organic top soil layer. Thus, the mean water flux from the organic top layer ( $Q$ ) can easily be estimated from annual means of precipitation ( $P$ ) and air temperature ( $T$ ), which are two traditional climate normals available in traditional climate maps (see Background document):

In European forest regions,  $Q_{le,zb}$  is typically  $0.1\text{--}0.6 \text{ m a}^{-1}$ , but may reach  $>2 \text{ m a}^{-1}$  in coastal mountain regions. The standard parameter uncertainty is on the order of  $\pm 0.1 \text{ m a}^{-1}$  (i.e. about  $\pm 30\%$ ) at the landscape scale. Depending on climate,  $Q_{le}$  can account for 10 to 90% of  $P$  in temperate-boreal forests, but is usually close to half. In very dry regions the percentage of  $Q_{le}$  in  $P$  can become very low. With eq. 5.91b,  $Q_{le}$  almost never drops below  $0.1 \text{ m}^{-1}$  in Europe (considering EMEP-50 km grid square means). For eq. 5.91a, a suggested minimum value is 5 % of the precipitation. This seems a reasonable lower value since there are always periods during the year with downward percolation and a situation of no leaching hardly (or never) occurs on a yearly basis. The use of monthly water balances is not advocated as the effect of all seasonal variations is not included in the critical limits, since these represent annual or long-term means, in line with the critical load approach for acidity.

### Critical total dissolved or total concentrations of heavy metals in soil drainage water

Information on the derivation of critical total dissolved concentrations of heavy metals in soil drainage water,  $[M]_{dis, \text{sdw(crit)}}$ , either directly, through transfer functions (plant -

soil solution) or through  $[M]_{free, \text{sdw(crit)}}$  is given in the next section (5.5.2.2), with background information on used approaches in the Annexes 1-3. The critical total dissolved metal concentrations related to ecotoxicological effects in soils require some specific considerations. These critical total metal concentrations in soil solution are determined as the sum of the critical concentration of the free metal ion  $M^+$ ,  $[M]_{free, \text{sdw(crit)}}$ , and the metals bound to dissolved inorganic complexes  $[M]_{DIC, \text{sdw}}$  such as  $MOH^+$ ,  $HCO_3^+$ ,  $MCl^+$ , and to dissolved organic matter,  $[M]_{DOM, \text{sdw}}$ , according to:

(5.92)

$$[M]_{dis, \text{sdw(crit)}} = [M]_{free, \text{sdw(crit)}} + [M]_{DIC, \text{sdw}} + [M]_{DOM, \text{sdw}} \cdot [DOM]_{\text{sdw}}$$

where:

$[M]_{dis, \text{sdw(crit)}}$  = critical total dissolved metal concentration in soil drainage water ( $\text{mg m}^{-3}$ )  
 $[M]_{free, \text{sdw(crit)}}$  = critical free metal ion concentration in soil drainage water ( $\text{mg m}^{-3}$ )  
 $[M]_{DIC, \text{sdw}}$  = concentration of metal bound to dissolved inorganic complexes in soil drainage water ( $\text{mg m}^{-3}$ )  
 $[M]_{DOM, \text{sdw}}$  = concentration of metal bound to dissolved organic matter in soil drainage water ( $\text{mg kg}^{-1}$ )  
 $[DOM]_{\text{sdw}}$  = concentration of dissolved organic matter in soil drainage water ( $\text{kg m}^{-3}$ )

Geochemical equilibrium partitioning of the heavy metal between the different fractions is assumed. Further, the water draining from the soil also contains metals bound to suspended particulate matter,  $[M]_{SPM, \text{sdw}}$ , according to:

(5.93)

$$[M]_{tot, \text{sdw(crit)}} = [M]_{dis, \text{sdw(crit)}} + [M]_{SPM, \text{sdw}} \cdot [SPM]_{\text{sdw}}$$

where:

$[M]_{tot, \text{sdw(crit)}}$  = critical total metal concentration in soil drainage water ( $\text{mg m}^{-3}$ )

$[SPM]_{sdw}$  = concentration of suspended particulate matter in soil drainage water ( $kg\ m^{-3}$ )

In the calculations, we suggest the particulate fraction to be neglected to get comparable values of critical concentrations for the different effects pathways (see Section 5.5.2.2.3). In this manual, the description of methods is adapted to the use of the critical total dissolved metal concentrations,  $[M]_{dis, sdw(crit)}$ , being equal to total metal concentrations in soil solution, implicitly assuming that the concentration of metals bound to suspended particulate matter is negligible ( $[SPM]_{sdw} = 0$ ), i.e.  $[M]_{dis, sdw(crit)}$  equals  $[M]_{tot, sdw(crit)}$ .

### 5.5.2.2 Critical dissolved metal concentrations derived from critical limits in terrestrial ecosystems

Critical total concentrations of the heavy metals *Cd*, *Pb* and *Hg* in the soil solution,  $[M]_{dis, sdw(crit)}$ , depend on the target to be protected. These values have to be derived from critical limits (see Table 5.17):

- Critical metal contents in plants (*Cd*, *Pb*, *Hg*) in view of human health or animal health effects through intake of plant products.
- Critical metal concentrations in ground water (*Cd*, *Pb*, *Hg*) in view of human health effects through intake of drinking water.
- Critical concentrations of free metal ions in soil solution (*Cd*, *Pb*) in view of ecotoxicological effects on soil micro-organisms, plants and invertebrates.
- Critical metal contents in the soil (*Hg*) in view of ecotoxicological effects on soil micro-organisms and invertebrates in the forest humus layer.

The critical total dissolved concentration of a heavy metal in the soil drainage water ( $[M]_{dis, sdw(crit)}$ ) includes both the free metal ions and the metals bound to dissolved inorganic and organic complexes (eq. 5.92).

The derivation of the critical total dissolved concentrations to be applied in eq. 5.90 is explained below.

#### 5.5.2.2.1 Critical dissolved concentrations of *Cd*, *Pb* and *Hg* in view of critical plant metal contents

Starting from the idea to derive critical total *Cd*, *Pb* and *Hg* concentrations in soil solution related to human health effects on the basis of critical limits for plant metal contents (food quality criteria) for food crops on arable land De Vries et al. (2003) provided an overview on selected soil-plant relationships of *Cd*, *Pb* and *Hg*. It shows that only for *Cd* significant relationships ( $R^2$  of  $\geq 0.5$ ) are available.

#### Cadmium

Starting with a critical *Cd* content in plant one may derive a critical dissolved metal concentration by a plant – soil solution relationship. Such a relationship was derived by applying a regression of *Cd* contents in wheat in the Netherlands to calculated soil solution concentrations, that were derived by using measured total soil contents and soil properties and application of a transfer function, relating total concentrations in solution to the soil metal content (Römkens et al. 2004). By applying such a function, regression relationships were derived for *Cd* in plant (wheat grains) as a function of *Cd* in soil solution and vice versa as described in Table 5.20. The best estimate of a critical *Cd* concentration might be the mean of both estimates.

The EU regulation (EG) No.466/2001 uses a limit for *Cd* of  $0.2\ mg\ kg^{-1}$  fresh weight in wheat grains. This limit was derived with the principle “As Low As Reasonably Achievable” (ALARA) and is therefore not based on effects. There are however many indications that from the viewpoint of protection of human health, the critical limit of  $0.1\ mg\ kg^{-1}$  fresh weight, which was used in the EU before 2001, is more appropriate (for these arguments see De Vries et al. 2003, 2005, 2007a). Table 5.20 provides

**Table 5.20.** Values for the intercept (int) and the parameter a in the regression relationships relating Cd in plant (wheat grains) as a function of Cd in soil solution and vice versa. The table also gives the percentage variation explained ( $R^2$ ), the standard error of the result (se) and the resulting critical total dissolved Cd concentration when applying a critical Cd content in wheat of  $0.1 \text{ mg kg}^{-1}$  fresh weight ( $0.12 \text{ mg kg}^{-1}$  dry weight) and in brackets the value when applying the limit of  $0.2 \text{ mg kg}^{-1}$  fresh weight (EG No 466/2001).

Relationship	Intercept	a	$R^2$	se	$\log[\text{Cd}]_{\text{dis, sdw(crit)}}$ [mmol.l <sup>-1</sup> ]	$[\text{Cd}]_{\text{dis, sdw(crit)}}$ [mg.m <sup>-3</sup> ]
$\text{Cd}_{\text{Plant}} - \text{Cd}_{\text{solution}}$ <sup>1</sup>	1.05	0.39	0.62	0.25	-5.03 (-4.26)	1.05 (6.16)
$\text{Cd}_{\text{solution}} - \text{Cd}_{\text{plant}}$ <sup>2</sup>	-3.82	1.57	0.62	0.50	-5.28 (-4.81)	0.59 (1.75)

<sup>1</sup>  $\log(\text{Cd plant}) = \text{Int} + a * \log(\text{Cd soil solution})$

<sup>2</sup>  $\log(\text{Cd soil solution}) = \text{Int} + a * \log(\text{Cd plant})$

the parameters for the transfer functions as well as results based on the critical limit of  $0.1 \text{ mg kg}^{-1}$  fresh weight (results for the EU limit of  $0.2 \text{ mg kg}^{-1}$  fresh weight is given in brackets). If the mean of both results of transfer function application is used, the resulting critical total concentration is approximately  $0.8 \text{ mg m}^{-3}$  (or  $4 \text{ mg m}^{-3}$ ). The most conservative estimate equals approximately  $0.6 \text{ mg m}^{-3}$  (or  $1.75 \text{ mg m}^{-3}$ ).

A more sophisticated and consistent way would be to

- first derive a critical "pseudo" total soil metal content, by applying soil – plant relationships in the inverse way (derive a critical total soil content from a critical plant content)
- then apply a transfer function relating "pseudo" total metal contents to reactive metal contents (Annex 1, eq. A1.3).
- followed by a transfer function relating the free ion metal activity in solution to the reactive metal content (Annex 1, eq. A1.4 or eq. A1.5).
- followed by a calculation of total concentrations from free metal ion activities with a chemical speciation model (i.e. the W6S-MTC2 model, Section 5.5.2.2.3).

Please note that the current version of W6S-MTC2 is designed to calculate  $M_{(\text{sdw})\text{crit}}$  based only on the critical limits relating to ecotoxicological effects and not to food quality.

### Lead and mercury

For Pb and Hg in food crops, back calculation to soil content is not possible, because there are no relationships between content of soil and contents in plants for those metals. For Pb and Hg, direct uptake from the atmosphere by plants has to be considered. Methods for such calculations, based on data from De Temmerman and de Witte (2003a,b) are provided in Annex 5 of the background document (De Vries et al. 2005).

#### 5.5.2.2.2 Critical dissolved concentrations of Cd, Pb and Hg aiming at ground water protection

The critical total Cd, Pb and Hg concentration in soil solution related to human health effects can also be based on quality criteria (critical limits) for drinking water (WHO 2004) for all terrestrial ecosystems (see Table 5.17). In line with the decisions of the Expert Meeting on Critical Limits (2002, in Berlin) the protection of ground water for potential use as drinking water resource should also be addressed in critical load calculations. The Technical Guidance Document for Risk Assessment (<http://ecb.jrc.it>) suggests in chapter 3.1.3 that in the first instance the concentration in soil pore water can be used as an estimate of the concentration in ground water. The WHO guideline includes the following quality criteria for Cd, Pb and Hg in view of drinking water quality:

Pb:  $10 \text{ mg m}^{-3}$

Cd:  $3 \text{ mg m}^{-3}$

Hg:  $1 \text{ mg m}^{-3}$

These values can directly be included as  $[M]_{dis, sdw(crit)}$  in the critical load calculation.

### 5.5.2.2.3 Critical dissolved concentrations of Cd and Pb related to ecotoxicological effects

Critical limits related to the ecotoxicological effects of *Cd* and *Pb* are related to impacts on soil micro-organisms, plants and invertebrates for both agricultural land (arable land, grassland) and non-agricultural land (forests, natural non-forested ecosystems; see Table 5.17). The critical concentrations used in this manual are based on the following approach:

- Use of ecotoxicological data (NOEC and LOEC data) for the soil metal content using experiments with information on soil properties (clay and organic matter content and soil *pH*) as well;
- Calculation of critical free metal ion concentrations (critical limits) in soil solution on the basis of the ecotoxicological soil data (NOECs and LOECs) and soil properties, using transfer functions relating the reactive soil metal content to the free metal ion concentration;
- Calculation of the critical total dissolved metal concentrations  $[M]_{dis, sdw(crit)}$  from critical limits for free metal ion concentrations using a chemical speciation model.

#### *Calculation of critical free metal ion concentrations from critical soil reactive metal contents*

Soil toxicity data collated and accepted under the terms of current EU Risk Assessment procedures (Draft Risk Assessment Report *Cd* (July 2003) see <http://ecb.jrc.it>, Voluntary Risk Assessment for *Pb*), were used. The data covered chronic population-level effects on soil plants, soil-dwelling invertebrates and microbial processes. The toxicity endpoints were quoted mainly in terms of an added metal dose. In using added doses, the assumption is made that the added metal is entirely in reactive forms over the course of the toxicity experiment.

The transfer functions for the calculation of free metal ion concentration from reactive soil metal content, used in the derivation of free ion critical limit functions, are given in Annex 1. Soil properties needed in this function are organic matter and soil solution *pH*. In the derivation, soil *pH* values measured by chemical extraction (by  $H_2O$ , *KCl* or  $CaCl_2$ ) were used to estimate soil solution *pH* by application of regressions given in Annex 10 of the background document (De Vries et al. 2004b), assuming that the *pH* in soil solution equals  $pH_{sdw}$ . EU Risk Assessment procedures do not require the organic matter content of the soil to be specified for data to be accepted. However, such data were not usable for the calculation of critical free metal ion concentrations from critical soil metal contents, since the used transfer functions do require these data (see Annex 1) and were thus removed from the databases.

The bioavailability of metals does not only depend on the free metal ion concentration but also on the concentration of other cations, particularly  $H^+$ . This was taken into account in deriving critical limits as a function of the *pH* in soil drainage water ( $pH_{sdw}$ ). The derived critical limit functions were:

(5.94)

$$\log[Cd]_{free, sdw(crit)} = -0.32 \cdot pH_{sdw} - 6.34$$

(5.95)

$$\log[Pb]_{free, sdw(crit)} = -0.91 \cdot pH_{sdw} - 3.80$$

More information on the approach and the toxicity data is given in Lofts et al. (2004) and in De Vries et al. (2004a). A summary can be found in the background document (De Vries et al. 2004b).

#### *Calculation of total dissolved metal concentrations from free metal ion concentrations*

To calculate critical loads for soils from the critical limit functions, it is necessary to know the total concentration of metal in soil

drainage water that corresponds to the free ion critical limit. In Annex 2, an overview is given of the calculation procedure using the WHAM model. Results thus obtained with this model for an assumed standard  $CO_2$  pressure of 15 times the atmospheric pressure of 0.3 mbar (4.5 mbar) are given in Tables 5.21 and 5.22. WHAM includes also the fraction of suspended particulate matter, which strictly is not part of the soil solution. The total concentration is therefore related to soil drainage water. When  $[SPM]_{sdw} = 0$ , the value of  $[M]_{tot, sdw(crit)}$  equals that of  $[M]_{dis, sdw(crit)}$  (see eq. 5.93). For reasons of consistency with the other approaches (see before), in which the critical value refers to  $[M]_{dis, sdw(crit)}$ , it is advocated to apply the results with  $[SPM]_{sdw} = 0$ . Furthermore, there are high uncertainties in the data on  $SPM$  in soil solution. Table 5.21 furthermore shows that in most cases, the impact of suspended

particulate matter on the total  $Cd$  concentration in soil drainage water (even at a concentration of  $50 \text{ mg l}^{-1}$ ) is small, but for  $Pb$  it can be large (Table 5.22).

### Use of $pH$ and $DOC$ values to be considered in the calculation of critical metal concentrations

Some parameters in the critical load calculation depend on the status of the soil, in particular the acidification status ( $pH$ ) and the concentration of  $DOC$  (see also the tables 5.21 and 5.22). In the following recommendations are provided, which status of soil conditions should be considered, when  $M_{dis, sdw(crit)}$  is derived from critical limits for free metal ion concentrations, as presented in the tables 5.21 and 5.22.

**Table 5.21:** Look-up table to derive values of the total critical  $Cd$  concentrations in soil drainage water  $[Cd]_{tot, sdw(crit)}$  at a  $CO_2$  pressure that equals 15 times the  $CO_2$  pressure of the air

OM %dw	SPM $\text{mg.l}^{-1}$	DOC $\text{mg.l}^{-1}$	[Cd] <sub>tot, sdw(crit)</sub> ( $\text{mg.m}^{-3}$ ), being [Cd] <sub>dis, sdw(crit)</sub> ( $\text{mg.m}^{-3}$ ) at SPM=0									
			pH 3.5	pH 4.0	pH 4.5	pH 5.0	pH 5.5	pH 6.0	pH 6.5	pH 7.0	pH 7.5	pH 8.0
10	0	0	4.04	2.79	1.92	1.34	0.94	0.68	0.51	0.43	0.47	0.75
10	0	5	4.04	2.80	1.93	1.38	1.04	1.08	0.91	0.66	0.61	0.80
10	0	15	4.04	2.81	1.97	1.47	1.23	1.83	1.68	1.13	0.88	0.91
10	0	50	4.05	2.86	2.12	1.80	1.89	4.08	4.03	2.74	1.85	1.30
10	0	100	4.07	2.94	2.36	2.29	2.80	6.76	6.86	4.94	3.22	1.85
10	50	0	4.06	2.82	1.95	1.38	1.00	0.76	0.61	0.57	0.67	1.02
10	50	5	4.06	2.82	1.96	1.42	1.10	1.16	1.02	0.81	0.80	1.07
10	50	15	4.06	2.84	2.00	1.51	1.29	1.91	1.79	1.28	1.08	1.18
10	50	50	4.07	2.89	2.15	1.85	1.94	4.15	4.14	2.88	2.05	1.57
10	50	100	4.08	2.96	2.39	2.33	2.85	6.84	6.97	5.08	3.42	2.12
50	0	0	3.98	2.74	1.91	1.34	0.94	0.68	0.51	0.43	0.47	0.75
50	0	5	4.02	2.81	2.02	1.52	1.26	1.09	0.91	0.66	0.61	0.80
50	0	15	4.11	2.94	2.24	1.89	1.85	1.86	1.68	1.13	0.88	0.91
50	0	50	4.45	3.48	3.01	3.06	3.69	4.16	4.03	2.74	1.85	1.30
50	0	100	5.06	4.29	4.07	4.59	5.96	6.89	6.86	4.94	3.22	1.85
50	50	0	4.03	2.81	2.00	1.45	1.11	0.90	0.81	0.84	1.03	1.51
50	50	5	4.07	2.87	2.10	1.64	1.42	1.31	1.21	1.08	1.17	1.57
50	50	15	4.16	3.00	2.32	2.01	2.01	2.08	1.98	1.54	1.44	1.68
50	50	50	4.50	3.54	3.09	3.18	3.85	4.38	4.33	3.15	2.41	2.06
50	50	100	5.11	4.35	4.16	4.71	6.12	7.11	7.16	5.35	3.78	2.61

## 5 Mapping Critical Loads

**Table 5.22:** Look-up table to derive values of the total critical Pb concentrations in soil drainage water  $[Pb]_{tot, sdw(crit)}$  at a  $CO_2$  pressure that equals 15 times the  $CO_2$  pressure of the air

OM %dw	SPM	DOC mg.l <sup>-1</sup>	[Pb] <sub>tot, sdw(crit)</sub> (mg.m <sup>-3</sup> ), being [Pb] <sub>dis, sdw(crit)</sub> (mg.m <sup>-3</sup> ) at SPM=0									
			pH	pH	pH	pH	pH	pH	pH	pH	pH	pH
10	0	0	34.72	11.41	3.83	1.32	0.46	0.17	0.08	0.09	0.23	0.72
10	0	5	34.80	11.55	4.02	1.57	0.77	0.86	1.12	1.29	1.36	1.64
10	0	15	34.96	11.83	4.42	2.09	1.38	2.18	3.16	3.67	3.61	3.47
10	0	50	35.52	12.82	5.83	3.92	3.42	6.25	10.04	11.87	11.47	9.89
10	0	100	36.33	14.25	7.92	6.51	6.21	11.39	19.36	23.30	22.68	19.07
10	50	0	37.33	14.50	7.43	5.53	5.41	5.98	6.88	8.08	9.60	11.71
10	50	5	37.41	14.64	7.62	5.79	5.72	6.66	7.92	9.27	10.73	12.63
10	50	15	37.57	14.92	8.02	6.31	6.33	7.98	9.97	11.66	12.98	14.46
10	50	50	38.13	15.91	9.43	8.14	8.37	12.05	16.84	19.86	20.84	20.89
10	50	100	38.94	17.34	11.52	10.74	11.16	17.19	26.17	31.29	32.05	30.06
50	0	0	32.85	11.08	3.80	1.31	0.46	0.17	0.08	0.09	0.23	0.72
50	0	5	34.36	12.59	5.32	2.74	1.63	0.89	1.12	1.29	1.36	1.64
50	0	15	37.41	15.65	8.37	5.51	3.80	2.25	3.16	3.67	3.61	3.47
50	0	50	48.44	26.65	18.69	14.44	10.52	6.45	10.04	11.87	11.47	9.89
50	0	100	65.13	42.22	32.86	26.13	18.94	11.76	19.36	23.30	22.68	19.07
50	50	0	39.22	18.51	12.51	11.53	12.45	14.27	16.57	19.45	22.94	27.36
50	50	5	40.73	20.03	14.03	12.96	13.63	14.95	17.61	20.64	24.06	28.27
50	50	15	43.78	23.08	17.07	15.74	15.78	16.30	19.66	23.03	26.31	30.11
50	50	50	54.80	34.07	27.42	24.65	22.51	20.51	26.54	31.24	34.18	36.53
50	50	100	71.49	49.66	41.61	36.34	30.92	25.82	35.86	42.66	45.38	45.70

**pH values:** In principle the pH at steady state conditions assuming Gothenburg Protocol implementation, can best be taken as a basis. This may cause problems, as it has to be determined using dynamic models. Instead the pH at the critical acid load can be used. This pH is easier to calculate but it may strongly deviate from the pH at steady state assuming Gothenburg Protocol implementation. Furthermore, the calculation of the critical load pH is rather uncertain depending on arbitrary choices to be made. Therefore the use of the critical load pH is not

recommended.

Assuming that it is likely that present pH is (almost) equal to future pH at steady state (under Göteborg Protocol implementation conditions), the present pH is advised to use for pragmatic reasons. Because the present pH in soil solution is not always available, but rather measured as pH in water or in salt extracts, regression functions to relate several pH measurements to soil solution pH were derived. Relations are given in Table 5.22, assuming no effect of soil type on the

**Table 5.23:** Results of linear regression analyses of the pH in soil solution against pH-H<sub>2</sub>O, pH-CaCl<sub>2</sub> and pH-KCl

Explaining variable	N	Slope ( $\alpha$ ) <sup>1)</sup>	Intercept ( $\beta$ ) <sup>1)</sup>	se <sub>Yest</sub>	R <sup>2</sup> adj
pH-H <sub>2</sub> O	1145	1.0462	-0.2847	0.453	0.84
pH-KCl	905	0.9692	0.6233	0.491	0.80

<sup>1)</sup> All coefficients are significant at  $p > 0.999$

relationship. These relations can be used to calculate the soil solution *pH* which is needed in the critical load calculations and also in the transfer functions relating reactive metal contents to free metal ion concentrations.

More detailed information is given in Annex 10 in the background document (De Vries et al. 2004b). This includes relationships as a function of soil type. Ranges in the present and steady-state critical soil *pH* for various combinations of land use, soil type and soil depth are also provided there.

***DOC* concentrations:** The concentration of dissolved organic matter (*DOM*) in soils is nowadays frequently determined in climate-related studies. Concentrations of *DOM* are usually determined by analysis of carbon (*DOC*) which accounts for half of the weight of soil organic matter ( $DOM = 2 \times DOC$ ). However, long-term data on soil solutions are rarely available at sufficient density for mapping region-specific means and variability's, and may need to be estimated from studies elsewhere. Ranges in *DOC* values for major forest types and soil layers, by means of the 5-, 50- and 95 percentiles, are presented in Annex 11 of the background document (De Vries et al. 2004b) on the basis of *DOC* values from approximately 120 Intensive Monitoring plots in Europe. In general, the results show a clear decrease in *DOC* concentrations going from the humus layer (median value of  $40 \text{ mg l}^{-1}$ ) into the mineral subsoil. Furthermore, the values are slightly higher in coniferous forest compared to deciduous forests.

Relationships of *DOC* concentrations with vegetation type, hydrology, growth conditions or soil properties may be expected, which would be useful to improve estimates for different sites and regions. The data for the mineral soil (De Vries et al. 2004b) were thus used to derive relationships with available site characteristics and soil data that may affect the *DOC* concentrations, including the type of forest, (coniferous or deciduous forests), texture class (indication for soil type), temperature, *pH* and the contents of *C* and *N*, including the *C/N* ratio. Results thus obtained are given in

the background document. The results show a good relationship with the site and soil characteristics in the subsoil (below 30cm) but the relationships were much worse in the topsoil (above 30cm). In the topsoil there was a clear positive relationship with *C/N* ratio and temperature, while the correlated values of the individual *C* and *N* concentrations were negatively and positively related to *DOC*, respectively. The relationships are, however, too weak to be very useful. This is in line with the limited number of studies in the literature, from which no significant relationship could be discerned (Michalzik et al. 2001).

Based on the available data the following default values for calculating critical loads of *Pb* and *Cd*, or critical levels of atmospheric *Hg* pollution, respectively, are suggested (see background document, Annex 11):

**Forest organic layer (O horizon):**

$$[DOC]_{sdw} = 35 \text{ mg l}^{-1} \quad ([DOM]_{sdw} = 70 \text{ mg l}^{-1}).$$

**Forest mineral topsoil (0-10 cm):**

$$[DOC]_{sdw} = 20 \text{ mg l}^{-1} \quad ([DOM]_{sdw} = 40 \text{ mg l}^{-1}).$$

**Grass land (0-10) cm:**

$$[DOC]_{sdw} = 15 \text{ mg l}^{-1} \quad ([DOM]_{sdw} = 30 \text{ mg l}^{-1}).$$

**Arable land (0-30) cm:**

$$[DOC]_{sdw} = 10 \text{ mg l}^{-1} \quad ([DOM]_{sdw} = 20 \text{ mg l}^{-1}).$$

### 5.5.2.2.4 Critical dissolved concentrations of *Hg* related to ecotoxicological effects in soils

***Critical limit for the soil:*** With respect to *Hg*, critical limits refer only to effects on soil micro-organisms and invertebrates in the humus layer of forests. The suggested critical limit for *Hg* is that the concentration in the humus layer (O-horizon) of forest soils after normalization with respect to the organic matter content should not exceed  $0.5 \text{ mg kg}^{-1} (\text{org})^{-1}$  (Meili et al. 2003a). Because of the strong association of *Hg* with organic matter leaving virtually no free ions, the exposure of biota to *Hg* is controlled by the

competition between biotic and other organic ligands, and the contamination of all types of organic matter is determined by the supply of organic matter relative to the supply of  $Hg$  at a given site (Meili 1991a, 1997, cf. biodilution). Therefore, the critical limit for  $Hg$  in soils is set for the organically bound  $Hg$  rather than for the free ion concentration, also in solution.

Critical total mercury concentrations in soil solution can be calculated by using a transfer function for  $Hg$  from soil to soil solution, while assuming a similar critical  $Hg/OM$  ratio in the solid phase and in the liquid phase, at least in oxic environments where binding to sulphides is negligible. Various reasons supporting this are given in Meili (1991a, 1997, 2003b), De Vries et al. (2003), and Åkerblom et al. (2004).

**Transfer function for mercury:** The critical leaching of  $Hg$  from the humus layer ( $M_{le(crit)}$ ) in eq. 5.88) is related to the mobility and  $Hg$  content of dissolved organic matter because of the strong affinity of  $Hg$  for living and dead organic matter and the resulting lack of competition by inorganic ligands in this layer (e.g. Meili 1991, 1997). Because of the strong association of  $Hg$  with organic matter leaving virtually no free ions (apparently far less than one per  $km^2$  of topsoil, based on Skyllberg et al. 2003), the biogeochemical turnover of  $Hg$  is controlled by the competition between biotic and other organic ligands. Therefore,  $Hg/OM$  ratios are a useful tool for calculating critical limits and loads and associated transfer functions (Meili et al. 2003a). This is the basis of the transfer function to derive total  $Hg$  concentrations in percolating (top)soil water ( $[M]_{dis, sdw(crit)}$ ) in eq. 5.90,  $mg\ m^{-3}$ ) as follows:

(5.96)

$$[Hg]_{dis, sdw(crit)} = [Hg]_{OM(crit)} \cdot f_f \cdot [DOM]_{sdw} \cdot c_{sdw}$$

where

$[Hg]_{dis, sdw(crit)}$  = critical total  $Hg$  concentration in soil drainage water ( $mg\ m^{-3}$ )

$[Hg]_{OM(crit)}$	= critical limit for $Hg$ concentration in solid organic matter ( $OM$ ), or the $Hg/OM$ ratio in organic (top)soils ( $[Hg]_{OM(crit)} = 0.5\ mg\ (kg\ OM)^{-1}$ ).
$f_f$	= fractionation ratio, describing the $Hg$ contamination of organic matter in solution ( $DOM$ ) relative to that in solids ( $OM$ ) (-),
$[DOM]_{sdw}$	= concentration of dissolved organic matter in soil drainage water ( $g\ m^{-3}$ ),
$c_{sdw}$	= $10^3\ kg\ g^{-1}$ , factor for appropriate conversion of mass units.

The scale-invariant fractionation or transfer factor  $f_f$  describes the  $Hg$  partitioning between organic matter in solids and organic matter in solution and is defined as the ratio between the  $Hg$  content of  $DOM$  and that of  $OM$  (Meili et al. 2003a, Meili et al. 2003b). Preliminary studies in Sweden suggest that the  $Hg$  concentration in  $DOM$  is of similar magnitude as that in  $OM$ , and that 1 may be used as a default value for  $f_f$  until deviations from unity prove to be significant (Åkerblom et al. 2004).

**Critical concentration for the soil drainage water:** Based on the  $Hg$  limit of  $0.5\ mg\ kg^{-1}$   $OM$  and a  $DOM$  concentration of  $70\ mg\ l^{-1}$  ( $DOC = 35\ mg\ l^{-1}$ ), the critical steady state concentration of total  $Hg$  in soil drainage water is  $35\ ng\ l^{-1}$  or  $0.035\ \mu g\ l^{-1}$  (see eq. 5.96). This concentration is consistent with that derived by a different approach at the watershed scale (Meili et al. 2003a) and is similar to high-end values presently observed in soil solutions and surface freshwaters (Meili, 1997; Meili et al. 2003b; Åkerblom et al. 2004). Note that this ecosystem limit for soil water is much lower than the drinking water limit above, but still higher than that for surface freshwaters where  $Hg$  limits for fish consumption usually are exceeded at surface water concentrations of  $1-5\ ng\ l^{-1}$ .

### 5.5.3. Aquatic ecosystems

#### 5.5.3.1 Critical loads of cadmium and lead

##### 5.5.3.1.1 Simple steady-state mass balance model and related input data

In principle, the simple steady-state mass balance approach can be used for *Cd*, *Pb* and *Hg* but it has been decided to restrict the approach in first instance to *Cd* and *Pb* and use a different, precipitation based approach for *Hg*, as described in Section 5.5.3.2.

##### Steady-state mass balance model in stream waters

As with terrestrial ecosystems, the critical load of *Cd* and *Pb* for freshwaters is the acceptable total load of anthropogenic heavy metal inputs corresponding to the sum of tolerable outputs from the catchment by harvest and outflow, minus the natural inputs by weathering release in the catchment but adding the retention in the surface water (De Vries et al. 1998). There is no need to consider net release in catchment soils, if the net weathering (weathering minus occlusion) is negligible. Since the estimation of net release in soils includes high uncertainties, it is preliminarily assumed to be negligible.

In the initial manual on the calculation of critical loads of heavy metals for aquatic ecosystems (De Vries et al. 1998), the default method presented to calculate critical loads of heavy metals for soils included in-lake metal retention, including all relevant metal fluxes, namely sedimentation, resuspension and exchange processes in the lake (infiltration, diffusion and bioirrigation), while assuming a steady state situation (DeVries et al.1998). To keep the approach as simple as possible, and also to stay as close as possible to the simple mass balance approach for nitrogen and acidity, this model can be simplified by neglecting weathering in the catchment and lumping transient exchange processes at the sediment-water interface and the net effect of sedimentation and resuspension in one retention term

according to De Vries et al. (1998):

(5.97)

$$CL(M) = M_u + M_{ret(crit)} \cdot \frac{A_l}{A_c} + M_{lo(crit)}$$

where:

$M_u$	= removal of heavy metal by biomass harvesting or net uptake in the catchment ( $g\ ha^{-1}a^{-1}$ )
$M_{ret(crit)}$	= net retention of heavy metal in the lake at critical load ( $g\ ha^{-1}a^{-1}$ )
$M_{lo(crit)}$	= critical lateral outflow of heavy metal from the whole catchment ( $g\ ha^{-1}a^{-1}$ )
$A_l$	= lake area ( $ha$ )
$A_c$	= catchment area ( $ha$ )

When critical loads of *Cd* and *Pb* for stream waters are calculated, there is no need to consider net retention, leading to the following critical load calculation:

(5.98)

$$CL(M) = M_u + M_{lo(crit)}$$

Because the estimation of net retention for lakes includes high uncertainties, it is recommendable to calculate preliminarily aquatic critical loads for stream waters only, for which the retention in surface water is negligible. It furthermore leads to the lowest critical loads and thus implies the protection of lakes as well. Finally, when calculating critical loads for lakes, one may also assume that net retention of metals in lakes is negligible, implying the assumption that the overall release or retention of metals in a catchment, including the lake sediment, is negligible.

##### Heavy metal removal by net uptake

The assessment of these data is comparable for those in terrestrial ecosystems (see eq. 5.89), but now the uptake or release refers to the complete catchment. This implies that no further reduction factors need to be applied to relate the uptake in the

root zone/catchment to the mineral topsoil. The equation for net uptake is thus equal to eq. 5.89 with  $f_{Mu}$  being equal to 1.

### Critical output of heavy metals from the aquatic system

The critical lateral outflow can be described as the product of the lateral outflow flux of water and the critical limit for the total concentration of the heavy metal in the surface water according to:

(5.99)

$$M_{lo(crit)} = 10 \cdot Q_{lo} \cdot [M]_{tot,sw(crit)}$$

where:

$Q_{lo}$	= lateral outflow flux of water from the whole catchment area ( $m^3 a^{-1}$ )
$[M]_{tot,sw(crit)}$	= critical limit for the total concentration (dissolved and in suspended particles) of heavy metal in surface water ( $mg m^{-3}$ )

$Q_{lo}$ , which sometimes is denoted as the hydraulic load in the literature can be derived for a lake on the basis of the flow from the aquatic system,  $Q$  ( $m^3 a^{-1}$ ) divided by the catchment area ( $m^2$ ). The total concentration of metals can be calculated as:

(5.100)

$$[M]_{tot,sw(crit)} = [M]_{dis,sw(crit)} + [M]_{SPM,sw(crit)} \cdot [SPM]_{sw}$$

where:

$[M]_{dis,sw(crit)}$	= critical dissolved concentration of a heavy metal in surface water ( $mg m^{-3}$ )
$[M]_{SPM,sw(crit)}$	= critical total content of a heavy metal in suspended particles ( $mg kg^{-1}$ )
$[SPM]_{sw}$	= concentration of suspended particulate matter in surface water ( $kg m^{-3}$ )

Data on the lateral outflow of lakes can be derived from the S&N critical loads

database. The critical load depends on the critical limit used. In the initial manual for aquatic ecosystems (De Vries et al. 1998), it was argued that critical limits referring to the free metal ion activity in surface water are most appropriate. This idea has been further developed by Lofts et al. (unpublished data), but has not been adopted here, for reasons which will be given in 5.5.3.1.2. Instead, critical limits referring to total dissolved metal concentrations have been adopted. It is necessary to include a solid-solution transfer function (see Annex 1) to calculate the critical metal concentration in suspended particles and hence the critical total aqueous metal concentration.

Information on how to estimate the critical net in-lake retention when calculating critical metal loads for lakes is given in the background document to this manual (De Vries et al. 2004b). Like for terrestrial ecosystems it is recommendable to calculate weathering rates (here at least for a depth of 1 m) to account for the influence of natural processes in comparison to atmospheric deposition in order to evaluate critical loads and critical limits exceedances. Information on how to calculate weathering within the catchment is given in Annex 6 of the background document.

### 5.5.3.1.2 Critical total dissolved cadmium and lead concentrations in aquatic ecosystems

#### Critical limits for total dissolved concentrations

Analysis of aquatic ecotoxicological data by Lofts et al. (unpublished) suggested overlap between aquatic and terrestrial toxic endpoint concentrations at a given pH. Hence it was suggested that common critical limits be applied for both soils and freshwaters, by using the critical limit functions derived in 5.5.2.2 for toxic effects on the soil ecosystem. However, although there is no theoretical reason why the sensitivities of soil and water organisms to metals should not be similar (assuming that uptake of the free ion from the aqueous phase is the

significant mechanism leading to toxicity) this approach has not been adopted for the following reasons:

1. The aquatic toxicity data for *Cd* covered a more restricted *pH* range than for the terrestrial toxicity data (*pH* 6.9 to 8.7 compared to *pH* 3.2 to 7.9). Therefore, although overlap of points was seen within the *pH* range covered by the aquatic toxicity data, no data were available to validate the theory of overlap below *pH* 6.9.
2. Observed overlapping of points for *Pb* was less than for any of the metals studied (*Cu* and *Zn* in addition to *Cd* and *Pb*). Most of the aquatic toxicity data gave free *Pb* endpoints higher than those observed for soils.

For these reasons, it was decided not to use the free ion approach for aquatic critical limits and instead to express the critical limits as the total dissolved metal ( $\text{mg m}^{-3}$ ). A summary of preliminary effect-based critical limits is given in Table 5.24. The values for *Cd* are based on the EU Risk Assessment Report for *Cd* (Risk assessment Cadmium metal CAS-No. 7440-43-9). The values for *Pb* are based on Crommentuijn et al. (1997) for the value suggested for use in the 2004 call for data, and on a substance data sheet on *Pb* and its compounds (2003) for the value to be used when updated Annex 3 is available. The reason of needing an update of Annex 3 is described below. The suggested substitute for Annex 3 is provided in Annex 12 of the background

document (DeVries et al. 2004b) including detailed calculation examples. The values are all related to ecotoxicological effects. There are also critical limits related to secondary poisoning, but these values are not yet recommended for use because they do require further substantiation and discussion.

The value of  $0.38 \text{ mg m}^{-3}$ , taken from EU Risk Assessment Report for *Cd*, is based on the 5-percentile cut-off value of chronic toxicity data from 168 reliable tests on single species and 9 multi-species studies. An assessment factor of 2 is further introduced in the report, leading to a critical limit of  $0.19 \text{ mg m}^{-3}$ , but this approach was not accepted in this manual. For *Cd*, a relationship with water hardness has also been found. In the EU Risk Assessment Report. Recently, it was also accepted to take the influence of hardness on the toxicity of cadmium into account, using 3 hardness classes (with hardness *H* in  $\text{mg CaCO}_3 \text{ l}^{-1}$ ) according to  $0.16 \text{ mg m}^{-3}$  if  $H < 100$ ,  $0.30 \text{ mg m}^{-3}$  if  $100 < H < 200$  and  $0.50 \text{ mg m}^{-3}$  if  $H > 200$ , using no assessment factor (see also the background document to the manual).

For *Pb*, the critical limit of  $11 \text{ mg m}^{-3}$  is based on Crommentuijn et al. (1997), whereas the value of  $5 \text{ mg m}^{-3}$  (range of  $2.1\text{--}9.3 \text{ mg m}^{-3}$ ) is based on the 5-percentile cut-off value of chronic toxicity data, calculated with the method of Aldenberg & Jaworska, using 3 data sets of selected (i) freshwater and saltwater NOECs/EC10s (30 values), (ii)

**Table 5.24:** Recommended critical limits for dissolved *Cd* and *Pb* concentrations surface waters

Metal	Critical dissolved concentration ( $\text{mg m}^{-3}$ )	
	Value to be used now	Value to be used when updated Annex 3 is available
Cd	0.38 <sup>1</sup>	0.16 if <i>H</i> < 100 <sup>2</sup> 0.30 if $100 < H < 200$ and 0.50 if <i>H</i> > 200
Pb	11	5

<sup>1</sup> A comparable critical limit is suggested in the RAR on *Cd* for the protection of top predators, namely  $0.26 \text{ mg m}^{-3}$ . This value is based on a critical limit for the intake of *Cd* of  $160 \mu\text{g Cd/kg}$  food (wet weight) of the predator, being the quality standard for biota tissue with respect to secondary poisoning. However, this value is yet considered too uncertain to be used in the critical load calculations

<sup>2</sup> *H* = hardness in  $\text{mg CaCO}_3 \text{ l}^{-1}$

freshwater NOECs/EC10s (19 values) and (iii) saltwater NOECs/EC10s (11 values). In the substance data sheet on *Pb*, an assessment factor of 3 is further introduced, but this approach was not accepted in this manual. At a workshop of ICP Waters on heavy metals, 2002, in Lillehammer (Skjelkvale and Ulstein, 2002) a range of 1 - 11 mg m<sup>-3</sup> was suggested in dependence on water chemistry, with low values referring to clear softwaters. The critical limit of 5 mg m<sup>-3</sup> is in the middle of this range and thus consistent. A much lower critical limit is suggested in substance data sheet on *Pb* for the protection of human health using a critical limit of 200 µg *Pb* kg<sup>-1</sup> muscle meat of fish (food standard set by Commission Regulation (EC) No. 466/2001) and the protection of predators in freshwater and saltwater environments from secondary poisoning (near 0.4 µg *Pb* l<sup>-1</sup>). However, this value is yet considered to uncertain to be used in the critical load calculations.

Although not presently used, a preliminary critical limit for *Hg* can be found in the substance data sheet on *Hg* and its compounds (2003). As with *Pb*, this value is based on the 5-percentile cut-off value of chronic toxicity data, using 3 data sets of selected (i) freshwater and saltwater, (ii) freshwater and (iii) saltwater, leading to a value of 0.142 mg m<sup>-3</sup> (90 percentile range of 0.056 - 0.281 mg m<sup>-3</sup>). In the substance data sheet on *Hg*, an assessment factor of 4 is further introduced, but this approach was not accepted in this manual. A reliable quality standard to protect top predators from secondary poisoning can not be given, but the value is much lower than those for ecotoxicological effects. The value of 0.035 mg m<sup>-3</sup> presented earlier for soils is likely to be an upper limit for secondary poisoning.

### *Calculation of critical limits for total aqueous concentrations*

In order to calculate critical loads of metals for freshwater ecosystems it is necessary to know the total aqueous concentration at the critical limit, i.e. the concentration of dissolved metal and of metal bound to

suspended particulate matter (*SPM*). There are various possible approaches to derive adsorbed metal contents on suspended particles ( $[M]_{SPM,sw}$ ) from total dissolved metal concentrations in surface water ( $[M]_{tot,sw}$ ). The simplest approach is a empirical linear approach ( $K_d$ -value) relating both contents and concentrations, while accounting for the impact of major properties of the suspended particles influencing the sorption relationship. However,  $K_d$  values for a given metal may vary substantially from place to place and so the  $K_d$  approach is not appropriate when calculating metal contents on suspended particles from a large number of different locations.

An alternative approach, which uses as far as possible data and models used elsewhere in this manual, is to take a two-stage approach:

1. Calculate the critical free ion concentration from the critical dissolved metal concentration.
2. Calculate the critical particle-bound metal from the critical free ion.
3. Sum the critical particle-bound and dissolved metal to obtain the critical total metal.

Step 1 uses a complexation model (e.g WHAM) to calculate the critical free ion concentration from the critical dissolved metal concentration. Step 2 uses a transfer function to calculate the particle-bound metal from the free ion. This transfer function is given in Annex 2. The calculation of the critical total aqueous concentration is presented in Annex 3.

In Annex 3, the procedure given applies only to the values of 0.38 mg m<sup>-3</sup> for *Cd* and 11 mg m<sup>-3</sup> for *Pb*. Use of different values (for *Cd* as a function of hardness and for *Pb* 5 instead of 11 implies a rerun of the WHAM model. This will be done and these values can be used, as soon as the updated Annex 3 is adopted.

### Surface water chemistry data

Data needed to calculate the total dissolved metal concentration are the concentration of suspended particles in the water compartment,  $[SPM]_{sw}$ , the  $pH$  and  $DOC$  concentrations of surface water. The concentration of  $SPM$  in the surface water ( $kg\ m^{-3}$  or  $g\ l^{-1}$ ) depends on the turbulence of the water, which in turn depends on the geological setting (incl. land use) and water flow velocity (i.e. wind speed for lakes). The concentration of suspended particles may thus vary considerably and generally ranges from 1 to  $100\ g\ m^{-3}$ . The average concentration for Dutch surface waters, for example, is  $30\ g\ m^{-3}$ , and for a dataset of lowland UK rivers ( $n = 2490$ ) it is  $30.6\ g\ m^{-3}$  with a range of  $<0.1$  to  $890\ g\ m^{-3}$ , while Scandinavian waters typically show much lower values.

$pH$  and  $DOC$  values for lakes largely depend on the landscape surrounding the lakes including the parent material (its sensitivity to acid inputs). Typical  $DOC$  values for clear water lakes are below  $5\ mg\ l^{-1}$ , whereas for humic lakes, values can be higher than  $50\ mg\ l^{-1}$ . Values for the  $pH$  generally vary between 5 and 7. Both  $pH$  and  $DOC$  are standard measurements in lake surveys and a wealth of data can be derived from those surveys.

When calculating in-lake retention in deriving critical loads for lakes, data on characteristics such as the lake and catchment area and the net retention rate are needed. For more information we refer to the background document (De Vries et al. 2004b) and an earlier manual (De Vries et al. 1998).

### 5.5.3.2 Critical levels of mercury in precipitation

Critical loads of atmospheric pollution for aquatic ecosystems (lakes and rivers) may be approached by a mass balance approach involving a wide variety of processes both within the water column and in the surrounding watershed. Alternatively, the steady state

partitioning of pollutants in a constant environment can be formulated without any need for mass balance considerations or detailed understanding of ecosystem processes. This can be achieved by linking critical receptors such as fish directly to the main immissions through transfer functions (TF) describing the relationship of their  $Hg$  concentrations at steady state, as described below.

#### 5.5.3.2.1 Derivation of critical levels of mercury in precipitation referring to a standard fish

##### Basic concept

$Hg$  concentrations in fish show a wide variation, about 30-fold both within and among sites (Meili 1997). A standardized value for a given site (lake or river) can be obtained by referring to a commonly caught piscivorous fish with a total body weight of 1 kg, in particular pike (*Esox lucius*). Using a 1-kg pike as a standard receptor, the mean  $Hg$  concentration in fish flesh can be related to the mean  $Hg$  concentration in precipitation at a given site as follows:

##### (5.101)

$$[Hg]_{Pike} = c_{bp} \cdot [Hg]_{Prec} \cdot TF_{HgSite}$$

where:

$[Hg]_{Pike}$  =  $Hg$  concentration in the flesh of 1-kg pike ( $mg\ kg^{-1}\ fw$ )

$[Hg]_{Prec}$  =  $Hg$  concentration in precipitation ( $ng\ l^{-1}$ )

$TF_{HgSite}$  = site-specific transfer function ( $l\ kg^{-1}\ fw$ ) referring to the transfer of atmospheric  $Hg$  to fish flesh in a watershed at steady state

$c_{bp}$  =  $10^{-6}\ mg\ ng^{-1}$ , factor for appropriate conversion of units.

The critical level of atmospheric pollution ( $[Hg]_{Prec(crit)}$ ) can thus be calculated as follows:

(5.102)

$$[Hg]_{Prec(crit)} = \frac{[Hg]_{Pike(crit)}}{(TF_{HgSite} \cdot c_{bp})}$$

where:

$[Hg]_{Pike(crit)}$  = critical Hg concentration in the flesh of 1-kg pike  
( $0.3 \text{ mg kg}^{-1} \text{ fw}$ )

$[Hg]_{Prec(crit)}$  = critical Hg concentration in precipitation ( $\text{ng l}^{-1}$ )

$c_{bp}$  =  $10^{-6} \text{ mg ng}^{-1}$ , factor for appropriate conversion of flux units.

Regarding the critical limit for mercury in pike of  $0.3 \text{ mg kg}^{-1} \text{ fw}$ , we refer to the background document of the manual (De Vries et al. 2004b).

*The transfer function  $TF_{HgSite}$*

$TF_{HgSite}$  addresses the wide variation of Hg concentrations among ecosystems in response to a given atmospheric Hg input at steady state. It accounts for a variety of complex processes including both terrestrial and aquatic aspects related to the biogeochemistry of Hg in lakes and rivers (Meili et al. 2003a), thus accounting for both fluxes and transformations of Hg (e.g. sorption, volatilization, net methylation, bioavailability, biodilution, biomagnification). For mapping of watershed sensitivity,  $TF_{HgSite}$  is preferably expressed as a function of basic physical-chemical parameters. Hg concentrations in fish are generally highest in nutrient-poor softwaters in acidic watersheds rich in wetlands (e.g. Verta et al. 1986, Håkanson et al. 1988, Meili 1991a, 1994, 1996a, 1997). Such differences can be described by empirical relationships to address regional and local differences in watershed biogeochemistry, based on variables for which data are commonly available (e.g. from other studies under CLRTAP), such as surface

water  $pH$  or concentrations of organic carbon or nutrients (the latter being of particular relevance for mercury). Two alternative formulations capturing part of the large variation in  $TF_{HgSite}$  are:

(5.103a)

$$TF_{HgSite} \approx \frac{TF_{HgRun} \cdot ([TOC]_{sw} + 1)}{(400 [TP]_{sw} + 6)}$$

(5.103b)

$$TF_{HgSite} \approx TF_{HgRun} \cdot e^{-\frac{(pH_{sw}-6)}{2}}$$

where:

$[TOC]_{sw}$  = concentration of total organic carbon in surface water ( $\text{mg l}^{-1}$ )

$[TP]_{sw}$  = concentration of total phosphorus in surface water ( $\text{mg l}^{-1}$ )

$pH_{sw}$  =  $pH$  in surface water

$TF_{HgRun}$  = transfer function ( $\text{l kg}^{-1} \text{ fw}$ ) referring to the transfer of atmospheric Hg to fish flesh via runoff in a reference watershed at steady state.

The first formulation (16a) is most appropriate and should be used when concentrations of total organic carbon and total phosphorus in surface water are available, which is often the case from routine monitoring of surface waters. The alternative formulation based on  $pH$  alone (16b) is less adequate but can be used if data access is limited.

$TF_{HgRun}$  can be quantified from adequate data sets in various ways (see Annex 13 of the background document, De Vries et al. 2004b). If such data are not available, a value of  $250\ 000 \text{ l kg}^{-1} \text{ fw}$  can be used for  $TF_{HgRun}$  referring to the standard fish (1 kg, in particular pike, *Esox lucius*) at steady state (Meili et al. 2003a, cf. Verta et al. 1986, Meili 1991a). An important aspect to consider when quantifying  $TF_{HgRun}$  (or other steady state parameters) from field data is that present environmental Hg concentrations are not in steady state with the present level of atmospheric pollution.

### 5.5.3.2.2 Derivation of critical levels of mercury in precipitation referring to other organisms

#### Basic concept

The  $Hg$  concentration in any fish or other organism, serving as food for humans and fish-based wildlife such as birds and mammals, can be related to the  $Hg$  concentration in 1-kg pike according to:

$$(5.104) \quad [Hg]_{Bio} = [Hg]_{Pike} \cdot TF_{HgBio}$$

where:

$[Hg]_{Bio}$  =  $Hg$  concentration in any biota, e.g. fish flesh ( $mg\ kg^{-1}\ fw$ )

$TF_{HgBio}$  = organism-specific transfer function addressing the typical  $Hg$  partitioning within food webs (-)

The critical level of atmospheric pollution ( $[Hg]_{Prec(crit)}$ ) can thus be calculated from a combination of eq. 5.102 and eq. 5.104 as follows:

$$(5.105) \quad [Hg]_{Prec(crit)} = \frac{[Hg]_{Bio(crit)}}{(TF_{HgBio} \cdot TF_{HgSite} \cdot c_{bp})}$$

where:

$[Hg]_{Bio(crit)}$  = critical  $Hg$  concentration in any biota, e.g. fish flesh ( $mg\ kg^{-1}\ fw$ )

$c_{bp}$  = see above

$TF_{HgBio}$  is useful for two purposes:

- (1) to estimate values for 1-kg pike for sites/regions in which only mercury concentrations in other organisms are available, (2) to convert critical load maps referring to 1-kg pike into maps for other target organisms of local/regional interest.

#### The transfer function $TF_{HgBio}$

$TF_{HgBio}$  addresses the wide variation of  $Hg$  concentrations among organisms within

food webs, by describing the typical deviation from the standard fish. Among commonly available variables, body weight is the most powerful single predictor of fish  $Hg$  levels, also across species. The variation in  $TF_{HgBio}$  can be described as follows:

(5.106)

$$TF_{HgBio} \approx f_{HgY} + f_{HgW} W^{2/3}$$

where:

$f_{HgY}$  = value for very young fish and other small animals (-);  $f_{HgY} \approx 0.13$

$f_{HgW}$  = species-specific slope coefficient (-);  
 $f_{HgW} \approx 0.2...2$  (Table 5.25)

$W$  = total body fresh weight ( $kg\ fw$ )

For many freshwater fish used for human consumption, this will generate estimates of mean  $Hg$  concentrations at a given fish size that differ less than 2-fold from observed means. Species-specific slope coefficients ( $f_{HgW}$ ) for some common freshwater fish are given in Table 5.25 for the typical case that the value for very young fish and other small animals ( $f_{HgY}$ ) can be maintained at 0.13. For any fish species (e.g. for unexplored sites or for unknown future fish populations), a first approximation differing less than 3-fold from observed size-class means can be made based on body weight alone, using the parameter for the standard fish, pike ( $f_{HgW} = 0.87$ , Table 5.25). If fish weight data are not available, total body weight ( $W$  in kg) can be estimated from total body length by applying a species-specific shape factor ( $f_{LW}$ , Table 5.25) according to:

(5.107)

$$W \approx f_{LW} \cdot L^{3.1}$$

where:

$L$  = length of the fish (cm)

**Table 5.25:** Coefficients for size conversion ( $f_{LW}$ ) and normalization of Hg concentrations ( $f_{HgW}$ ) in freshwater fish, some standard fish weights (W) for consumption and the related value for  $TF_{HgBio}$

Fish taxa			$f_{LW}$	$f_{HgW}$	W	$TF_{HgBio}$
pike	<i>Esox lucius</i>	Esocidae	$3.8 \cdot 10^{-6}$	0.87	1.0	1.0
pike-perch, zander	<i>Stizostedion lucioperca</i>	Percidae	$6.4 \cdot 10^{-6}$	1.2	1.0	1.3
perch	<i>Perca fluviatilis</i>	Percidae	$7.9 \cdot 10^{-6}$	1.9	0.3	1.0
trout	<i>Salmo trutta</i>	Salmonidae	$7.2 \cdot 10^{-6}$	0.4	0.3	0.3
Arctic char	<i>Salvelinus alpinus</i>	Salmonidae	$6.8 \cdot 10^{-6}$	0.7	0.3	0.4
whitefish	<i>Coregonus spp.</i>	Coregonidae	$6 \cdot 10^{-6}$	<0.4...>2		
burbot	<i>Lota lota</i>	Lotidae	$5 \cdot 10^{-6}$	0.9	0.3	0.5
bream	<i>Abramis brama</i>	Cyprinidae	$8 \cdot 10^{-6}$	0.25	0.3	0.2
roach	<i>Rutilus rutilus</i>	Cyprinidae	$6.8 \cdot 10^{-6}$	0.6...1.2		

Table 5.25 is meant as a reference that can be expanded and adapted for local use, based on additional field data from systems where several coexisting species have been analyzed. Note that for compatibility of transfer functions and for inter-regional comparisons, the value of  $TF_{HgBio}$  refers to a 1-kg pike, which should be maintained as a reference receptor with a value of  $TF_{HgBio} = 1$ .

#### 5.5.4. Limitations in the present approach and possible future refinements

In general the uncertainties in measurement as well as in modelling are higher with respect to trace elements than for main nutrient elements. In particular the following uncertainties of the models should be mentioned:

-The steady-state of metal inputs and outputs on the level of the critical limit is a theoretical situation. In dependence of the actual status of a site (or area) it may take years to centuries (e.g. for calcareous soils) to reach this steady-state. This should be considered, when critical loads and their exceedances are to be interpreted. To consider the processes of metal accumulation or loss from soils over time, dynamic approaches would be needed. Although such models are already suggested, they are not yet considered here, because they still need further sophistication. There is some inconsistency between the calculation of the critical leaching and the tolerable removal of the

metals with biomass, because types of critical limits and their mode of use are different for both fluxes.

-The uptake of heavy metals by plants is not constant over time but varies strongly with changes in pollution and is at present likely lower than indicated above at steady state at the level of critical concentrations,

-Possible effects of thinning of the metal concentration due to high mass fluxes of biomass harvest (high yields) are not considered due to missing knowledge,

-The delivery of heavy metals to the available pools of soils and surface waters is excluded from the mass balance equation due to high uncertainties of the available calculation approach. However since the same approach is used to identify sites with high natural inputs it may happen that one site is excluded, while another site with an insignificant lower weathering rate will stay in the database,

-The approaches taken to calculate critical limits for ecotoxicological effects are different for terrestrial and aquatic ecosystems. Given the likelihood that terrestrial and freshwater organisms (with the exception of surface-dwelling soil invertebrates such as snails) are exposed to metal in a similar manner (i.e. via the solution phase), a common approach to deriving critical limits, if not common values or functions for the limits, is scientifically desirable,

- The critical limit derivation includes several uncertainties, as e.g. differences between results from laboratory or field, which are (deviating e.g. from OECD methodologies) not taken into account by the use of "uncertainty factors",
- Organisms can be affected by different pathways, this could only partly be considered here,
- The vertical flux of metals bound to particulate matter suspended in the drainage water, may be remarkable in certain soils, this holds in particular for *Pb*. It was, however, not recommended to consider this, in order to be consistent with other parts of the manual,
- The seasonal variation of soil parameters such as *pH*, *DOC* cannot be accounted for in the models.

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### Annex 1: Transfer functions for lead and cadmium for the conversion of metal concentrations in different soil phases

#### Need of transfer functions in deriving critical dissolved metal concentrations

In principle, transfer functions are not needed in performing a critical load calculation. Transfer functions have been used to derive critical limits for free metal ion concentrations from NOEC data, referring to reactive soil metal contents. When applying critical limits for free metal ion concentrations, related to ecotoxicological effects, no transfer function is needed any more, since  $[M]_{(sdw)crit}$  can be obtained directly, either by reference to the look up tables or by use of the W6S-MTC2 program (see Section 5.5.2.2.3). In case of ground water protection, total dissolved critical concentrations can be used directly (see Section 5.5.2.2.2). In the case of using critical limits referring to the metal content in plants, an empirical relationship can be used to derive total dissolved critical concentrations in soil solution, at least for *Cd* (See Table 4).

Using the more sophisticated and consistent way to derive soil solution concentrations from critical plant contents does however require transfer functions according to the following:

- first derive a critical “pseudo” total soil metal content, by applying soil-plant relationships in the inverse way (derive a critical total soil content from a critical plant content)
- then apply a transfer function relating pseudo- total metal contents to reactive metal contents (Annex 1, eq. A1.3).
- followed by a transfer function relating the free ion metal activity in solution to the reactive metal content (Annex 1, eq. A1.4 or eq. A1.5).

Furthermore, all the transfer functions listed

below are needed for the calculation of a critical soil limit (from a given critical limit function for the soil solution) and to compare this to the present soil metal content to assess the critical limit exceedance in the present situation. This requires a map of the present soil metal content in the country. Inversely, one may calculate the present dissolved metal concentration from the present soil metal content, using the transfer functions described below and compare this to the critical limit function for the soil solution (see section 5.5.1.4).

#### Transfer functions to calculate pseudo-total from total contents of *Cd* and *Pb*

In some countries true total metal concentrations are measured, whereas most or nearly all countries use “pseudo-total” concentrations. Utermann et al. (2000) provided transfer functions to calculate *pseudo-total* contents of heavy metals (here aqua regia extract  $[M]_{AR}$ ) from total contents (here  $[M]_{HF}$ ), according to:

(A1.1)

$$\log_{10}[M]_{AR} = a_0 + a_1 \cdot \log_{10}[M]_{HF}$$

where:

- $[M]_{HF}$  = total content of heavy metal *M* in soil, provided as *HF*-extraction ( $mg\ kg^{-1}$ )
- $[M]_{AR}$  = *pseudo-total* content of heavy metal *M* in soil provided as *Aqua Regia* extraction ( $mg\ kg^{-1}$ )

Values for  $a_0$  and  $a_1$  are given in Tables A1.1 and A1.2. The correlations are depending on metal and substrate. In general, total and *pseudo-total* contents are very similar. For back-calculations of total contents from *pseudo-total* contents, different functions are to be used (see background document, De Vries et al 2004b, Annex 7). These functions are not provided here, since those calculations are not needed in the present calculation of critical loads.

## 5 Mapping Critical Loads

**Table A1.1:** Relationship between cadmium (*Cd*) content in soils extractable by aqua regia (*AR*) and total contents in dependence on the parent material.

parent material	$a_0$	$a_1$	n	$R^2$	range of validity	
						Cd (HF) (mg kg <sup>-1</sup> )
basic and intermediate igneous rock	0.13	1.41	25	0.94	0,25	1,12
boulder clay	0.09	1.38	26	0.91	0.07	0.39
limestone	-0.15	1.24	25	0.91	0.26	1.86
loess or loessic loam	-0.15	1.26	25	0.91	0.07	0.88
marl stone	-0.05	1.24	25	0.93	0.10	0.98
sand	-0.02	1.26	37	0.89	0.04	0.65
sandy loess	0.29	1.78	36	0.82	0.06	0.29
acid igneous and metamorphic rock	-0.09	1.08	25	0.80	0.09	0.63
quartzitic sand stones and conglomerates	-0.11	1.23	25	0.81	0.07	0.60
clay stone, hard argillaceous and silty slates	-0.05	1.33	25	0.96	0.14	1.88
all parent materials	-0.12	1.19	274	0.91	0.04	1.88

**Table A1.2:** Relationship between lead (*Pb*) content in soils extractable by aqua regia (*AR*) and total contents extractable by *HF* in dependence on the parent material.

parent material	$a_0$	$a_1$	n	$R^2$	range of validity	
						Pb (HF) (mg kg <sup>-1</sup> )
basic and intermediate igneous rock	-0.20	1.11	25	0.97	5.6	113.6
boulder clay	-0.54	1.32	26	0.95	8.3	49.5
limestone	-0.02	0.99	22	0.88	24.8	132.7
loess or loessic loam	-0.42	1.22	24	0.91	15.1	91.8
marl stone	-0.03	0.95	25	0.94	5.5	124.0
sand	-0.54	1.31	49	0.91	2.7	76.7
sandy loess	-0.72?	1.46	43	0.97	6.0	75.9
acid igneous and metamorphic rock	-0.84	1.44	25	0.84	14.6	106.1
quartzitic sand stones and conglomerates	-0.55	1.28	25	0.88	12.6	109.2
clay stone, hard argillaceous and silty slates	-0.11	1.05	25	0.98	13.9	270.3
all parent materials	-0.45	1.24	289	0.95	2.7	270.3

*Transfer functions to calculate reactive contents from pseudo-total contents of Cd and Pb*

The reactive metal concentration  $[M]_{re}$  (mol kg<sup>-1</sup>) can be related to the *pseudo-total* concentration extracted with Aqua Regia  $[M]_{AR}$  (mol kg<sup>-1</sup>) according to:

(A1.3)

$$\log[M]_{re} = \beta_0 + \beta_1 \cdot \log[M]_{AR} + \beta_2 \cdot \log(\%[OM]_s) + \beta_3 \cdot \log(\%[clay])$$

Regression relations were derived from a Dutch dataset containing 630 soil samples which were both extracted with 0.43 Mol l<sup>-1</sup> *HNO<sub>3</sub>* and *Aqua Regia*. The dataset consists of large variety of soil types with a wide variety in soil properties such as the organic matter and clay content. The dataset comprises both polluted and unpolluted soils. Results are shown in Table A1.3 and suggest that reactive contents typically are more than half of *pseudo-total* contents.

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**Table A1.2:** Relationship between lead (*Pb*) content in soils extractable by aqua regia (*AR*) and total contents extractable by *HF* in dependence on the parent material.

Metal	$\beta_0$	$\beta_1$	$\beta_2$	$\beta_3$	$R^2$	se-yest <sup>1)</sup>
Cd	0.225	1.075	0.006	-0.020	0.82	0.26
Pb	0.063	1.042	0.024	-0.122	0.88	0.17

<sup>1)</sup> The standard error of the y-estimate on a logarithmic basis

**Transfer functions to calculate free Cd and Pb ion concentrations from reactive Cd and Pb contents used in the derivation of critical limits for free Cd and Pb ion concentrations**

Critical concentrations of soil metal are frequently higher than ambient soil concentrations. Therefore, a transfer function should if possible be calibrated over a range of soil metal concentrations which is the whole range of critical receptor concentrations observed. This is relevant since the derived critical limit functions are dependent upon the transfer functions.

For calibration of direct transfer functions for Cd and Pb, data were drawn from four sources:

- Sauvé et al. (1998). Soil metal and labile Pb in Pb-contaminated soils of various origins. Free Pb concentrations were estimated by measurement of labile Pb using differential pulse anodic stripping voltammetry (DPASV) and speciation calculations.
- Sauvé et al. (2000). Soil metal and labile Cd in Cd-contaminated soils of various origins. Free Cd concentrations were estimated by measurement of labile Cd using differential pulse anodic stripping voltammetry (DPASV) and speciation calculations.
- Weng et al. (2002). Soil metal and free ion concentrations in sandy Dutch soils.

Free Cd and Pb concentrations were estimated by the Donnan membrane technique.

- Tipping et al. (2003a). Soil metal and free ion concentrations in UK upland soils. Free Cd and Pb were estimated by using the WHAM6 speciation model (Tipping, 1998) to speciate the soil solution.

The data were fitted to the following transfer function (termed as c-Q relationship):

(A1.4)

$$\log[M]_{\text{free, sdw}} = a + b \cdot \log[\text{OM}]_s + c \cdot \text{pH}_{\text{sdw}} + m \cdot \log[M]_{\text{re}}$$

where:

$[M]_{\text{free, sdw}}$  = the free metal ion concentration ( $\text{mol l}^{-1}$ )

$[M]_{\text{re}}$  = the reactive metal content in the solid phase ( $\text{mol l}^{-1}$ )

$[\text{OM}]_s$  = organic matter (%)

$\text{pH}_{\text{sdw}}$  = soil drainage water pH

Calculated values of the parameters are given in Table A1.4.

**Table A1.4:** Values for the regression coefficients for the free ion concentration - reactive metal content relationship (eq. A1.4) and statistical measures  $R^2$  and  $\text{se}(Y)$  based on results of studies carried out in Canada, the Netherlands and the UK. Values in brackets are the standard errors for the coefficients.

Metal	a	b (OM) <sub>s</sub>	c (pH) <sub>sdw</sub>	m (log[M] <sub>re</sub> )	$R^2$	se(Y)
Cd	-0.08 (0.65)	-0.60 (0.08)	-0.53 (0.03)	0.60 (0.06)	0.624	0.53
Pb	4.32 (0.49)	-0.69 (0.07)	-1.02 (0.03)	1.05 (0.06)	0.854	0.60

**Transfer functions to calculate reactive Cd and Pb contents from free Cd and Pb ion concentrations used in the derivation of critical Cd and Pb contents on suspended particles in aquatic ecosystems**

This transfer function (termed as Q-c relationship) has been derived using the same soil data set used to calculate the transfer function relating the free ion to the soil reactive metal (See Table A1.4). The expression for the Q-c relation is:

$$(A1.5) \quad \log[M]_{re} = a + b \cdot \log[OM]_s + c \cdot pH_{sw} + m \cdot \log[M]_{free,sw}$$

where:

- $[M]_{free,sw}$  = the free metal ion concentration in surface water ( $mol l^{-1}$ )
- $[M]_{re}$  = the reactive metal content in the solid phase ( $mol l^{-1}$ )
- $[OM]_s$  = organic matter (%), here the organic matter content of the suspended particles
- $pH_{sw}$  = the pH of the surface water

Calculated values of the parameters are given in Table A1.5.

**Table A1.5:** Values for the regression coefficients for the reactive metal content - free ion concentration relationship (eq. 8) and statistical measures  $R^2$  and  $se(Y)$  based on results of studies carried out in Canada, the Netherlands and the UK. Values in brackets are the standard errors for the coefficients.

Metal	a	b ( $[OM]_s$ )	c ( $pH_{sw}$ )	m ( $\log[M]_{free,sw}$ )	$R^2$	$se(Y)$
Cd	-6.42 (0.41)	0.64 (0.07)	0.45 (0.04)	0.58 (0.06)	0.507	0.52
Pb	-5.42 (0.21)	0.55 (0.06)	0.70 (0.03)	0.61 (0.03)	0.698	0.45

### Use of transfer functions in the manual

The direct transfer function for the calculation of the free ion concentration from the soil reactive metal content (the c-Q relation) is used for the calculation of the pH-dependent critical limit functions (see Section 5.5.2.2.3), in order to express the endpoint metal dose in toxicity experiments as the free ion concentration. The transfer function for the calculation of the soil reactive metal content from the free metal ion concentration (the Q-c relation) is used to calculate the critical SPM-bound metal ( $[M]_{SPM} (crit)$ ) in surface waters (see Section 5.5.2.2.3 and Annex 2).

### Annex 2: Calculation of total metal concentration from free metal ion concentrations using the WHAM model

The metal in soil drainage water comprises the following metal species

Metal species	<u>Symbol</u>
Metal free ion $M^{2+}$	$[M]_{free, sdw}$
Inorganic complexes $MOH^+$ , $MHCO_3^+$ , $MCl^+$ etc	$[M]_{DIC, sdw}$
Metal bound to DOM	$[M]_{DOM, sdw}$
Metal bound to SPM	$[M]_{SPM, sdw}$

Here, *DOM* is dissolved organic matter, and *SPM* is suspended particulate matter. The total concentration of metal in soil drainage water does not refer simply to dissolved components ( $[M]_{free, sdw}$ ,  $[M]_{DIC, sdw}$ , and  $[M]_{DOM, sdw}$ ), but also includes  $[M]_{SPM, sdw}$ . Data on *SPM* concentration in soil drainage waters may be scarce, and in many cases the contribution of *SPM* to the metal leaching is only small. Thus this flux can be neglected preliminarily. The calculation model includes, however, the possibility of metal being leached from the soil in association with particulates.

Given the activity or concentration of  $M^{2+}$ , the concentrations of the other metal species can be estimated by applying an equilibrium speciation model. The calculation has to take into account the dependence of the metal speciation on *pH* and competitive effects due to major cationic species of *Mg*, *Al*, *Ca* and *Fe*. For this purpose a custom version of the Windermere Humic Aqueous Model version 6 (WHAM6; Tipping 1998) speciation model, termed W6S MTC2, has been produced. A more detailed description of the model calculation steps is given in the background document (De Vries et al. 2004b). NFCs may calculate critical dissolved metal concentrations from the free ion concentration by one of three methods:

1. Linear interpolation in the look-up tables (chapter 5.5.2.2.3). The look-up tables list critical dissolved metal concentrations (calculated using W6S-MTC2) for various combinations of *pH*, concentrations of soil organic matter, dissolved organic carbon ( $[DOC]_{sdw}$ ) and suspended particulate matter (*SPM*) and partial  $CO_2$  pressure ( $pCO_2$ ).

2. Sending suitably formatted files to the Centre for Ecology & Hydrology (CEH), Lancaster, Ed Tipping (ET@CEH.AC.UK), who will perform the computations with W6S-MTC2. Instructions for preparing suitably formatted files for this purpose are given below.

3. Using the W6S-MTC2 program themselves. Instructions for use are given with the program, which can be obtained by contacting Ed Tipping (see above).

NFCs that wish values of  $M_{tot, sdw(crit)}$  to be calculated by should submit files to the CEH Lancaster, Ed Tipping (ET@CEH.AC.UK). The data should simply be entered into an Excel workbook, under the following headings.

code	pH	% OM	pCO <sub>2</sub>	DOC	SPM
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code	the user's identifier of the site
pH	soil solution pH
% OM	the soil organic matter content
pCO <sub>2</sub>	the soil pCO <sub>2</sub> expressed as a multiple of the atmospheric value
DOC	concentration of dissolved organic carbon in mg l <sup>-1</sup>
SPM	concentration of suspended particulate matter in mg l <sup>-1</sup> .

- Please see the background document (Annex 8 and 9) regarding the selection of *pH* and *pCO<sub>2</sub>* values. If data on *DOC* concentration are not available, a standard value of 20 mg l<sup>-1</sup> will be assumed.

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- If data on  $pCO_2$  are not available, a value of 15 x atmospheric will be assumed.
- If data on  $SPM$  are not available, a value of zero will be assumed.

Please note that it is necessary to recalculate values of soil  $pH$  (measured in  $KCl$ ,  $CaCl_2$ ,  $H_2O$ ) to soil solution  $pH$ , as mentioned in the main text, before applying the look-up tables or creating input files for W6S-MTC2.

- **Annex 3: Calculation of critical total Cd and Pb concentrations in surface water related to ecotoxicological effects**

This Annex was first published as Appendix 12 of the background document (De Vries et al. 2005) and became part of the Manual by decision of the 22<sup>th</sup> Task Force on ICP Modelling and Mapping (April 2006, in Bled, Slovenia). It replaces the original version of Annex 3 (October 2004).

The calculation of the critical total aqueous concentration comprises the following steps:

1. Estimate the critical free metal ion concentration from the critical dissolved concentration (critical limit).
2. Calculate the metal bound per unit mass of suspended particulate matter (*SPM*).
3. Calculate the water hardness.
4. Sum the total dissolved and particulate concentrations.

### **Step 1**

The critical free metal ion concentrations ( $[M]_{free, crit}$ ) ( $mol\ l^{-1}$ ) are calculated using WHAM6, for waters of different  $pH$ ,  $DOC$  and  $pCO_2$ , making the same assumptions as are used for calculating total metal from free-ion critical limits (for the Look Up Tables, see 5.5.2.2.3). These assumptions also lead to hardness values ( $H$  = hardness in  $mg\ CaCO_3\ l^{-1}$ ). In the calculations the critical dissolved concentrations used depend on the water hardness in case of  $Cd$  ( $0.16\ mg\ m^{-3}$  if  $H < 100$ ,  $0.30\ mg\ m^{-3}$  if  $100 < H < 200$  and  $0.50\ mg\ m^{-3}$  if  $H > 200$ ), whereas a value of  $5\ mg\ m^{-3}$  was used for  $Pb$ . Note that, here, all waters are assumed to be “normal” with respect to dissolved  $Al$  (i.e. acid bog-waters are not included).

Free ion activities corresponding to these limits (taking into account the variation in the  $Cd$  critical limit with water hardness) were calculated with WHAM6 for a range of solution conditions covering most natural freshwaters. They can be expressed in terms of multiple regression equations at different  $pH$  values, according to:

$$\log [M]_{free,crit} = A \cdot [DOC] + B \cdot pCO_2 + C \quad (A3.1)$$

where  $[DOC]$  is in  $mg\ l^{-1}$  and  $pCO_2$  is a multiple of the atmospheric  $pCO_2$ . Root mean square errors in  $\log [M]_{free,crit}$  between the WHAM6 values and the regression values are  $< 0.12$  for  $Cd$  and  $< 0.18$  for  $Pb$ . The regression coefficients are given in Tables A3.1 and A3.2. Linear interpolation can be performed to obtain coefficients for intermediate  $pH$  values.

*Table A3.1 Regression coefficients for estimating critical free  $Cd^{2+}$  concentrations*

pH	A	B	C
4	-0.0004	0.0000	-8.87
5	-0.0053	-0.0001	-8.87
6	-0.0258	0.0040	-8.93
7	-0.0344	0.0189	-9.05
8	-0.0196	0.0466	-9.18
9	-0.0010	-0.0742	-9.44

Table A3.2 Regression coefficients for estimating critical free  $Pb^{2+}$  concentrations

pH	A	B	C
4	-0.0020	0.0000	-7.66
5	-0.0231	0.0000	-7.70
6	-0.0546	0.0062	-8.19
7	-0.0681	0.0261	-9.33
8	-0.0641	0.0349	-10.33
9	-0.0160	-0.1303	-11.41

### Step 2

The critical *SPM*-bound metal ( $[M]_{SPM(crit)}$ ,  $mol \cdot g^{-1}$ ) is calculated using the Q-c relations derived in Annex 1, eq. A1.4 (Table A1.4). In this way we do calculate the critical reactive metal content on the suspended particles. This is considered appropriate by limiting the critical load approach to processes and fluxes of geochemically reactive metals. This implies that actual loads should also be related to the reactive fraction of the total input. Deposition measurements practices aim at extraction of reactive species (not total metal). Therefore we assume that, since EMEP models are calibrated to measurements, the currently mapped concentration/ deposition data (called “total”) can be regarded as geochemically reactive metals.

Before proceeding to Step 3  $[M]_{SPM(crit)}$  must be converted to units of  $mg \cdot kg^{-1}$  by multiplying with the molar weight and a factor  $10^6$  to transfer from  $g \cdot g^{-1}$  to  $mg \cdot kg^{-1}$

$$[Cd]_{SPM(crit)} (mg \cdot kg^{-1}) = [Cd]_{SPM(crit)} (mol \cdot g^{-1}) \cdot (112 \cdot 10^6) \quad (A3.2a)$$

$$[Pb]_{SPM(crit)} (mg \cdot kg^{-1}) = [Pb]_{SPM(crit)} (mol \cdot g^{-1}) \cdot (207 \cdot 10^6) \quad (A3.2b)$$

### Step 3

Using the assumptions about water composition (see Step 1), water hardness ( $mg \cdot CaCO_3 \cdot l^{-1}$ ) is given by regression equations of the following form:

$$\text{hardness} = A \cdot [\text{DOC}] + B \cdot pCO_2 + C \quad (A 3.3)$$

where  $[\text{DOC}]$  is in  $mg \cdot l^{-1}$  and  $pCO_2$  is a multiple of the atmospheric  $pCO_2$ . The regression coefficients are given in Table A3.3. Linear interpolation can be performed to obtain coefficients for intermediate  $pH$  values.

Table A3.3 Regression coefficients for estimating water hardness

pH	A	B	C
4	0.00	0.00	0.00
5	0.11	0.02	-0.37
6	0.23	0.34	-0.14
7	0.31	3.4	-0.12
8	0.36	38.2	-6.84
9	0.43	1020	-966

#### Step 4

The total metal concentration in surface water at the critical limit is given by:

$$[M]_{\text{tot, sw(crit)}} = [M]_{\text{dis, sw(crit)}} + [M]_{\text{SPM (crit)}} \cdot [SPM]_{\text{sw}} \quad (\text{A3.4})$$

where  $[M]_{\text{dis, sw(crit)}}$  is the critical dissolved concentration ( $\text{mg m}^{-3}$  or  $\mu\text{g l}^{-1}$ ) (See Table 5.24 in the main text),  $[M]_{\text{SPM(crit)}}$  is the critical concentration bound to  $SPM$  calculated in Step 2 ( $\text{mg.kg}^{-1}$ ), and  $[SPM]_{\text{sw}}$  is the  $SPM$  concentration in surface water ( $\text{kg m}^{-3}$ ).

#### FULL CALCULATION EXAMPLE #1

pH	=	6
DOC	=	$8 \text{ mg l}^{-1}$
pCO <sub>2</sub>	=	4 times atmospheric
SPM	=	$50 \text{ mg l}^{-1}$
% OM	=	20

##### Step 1

$$\begin{aligned} \log [Cd]_{\text{free(crit)}} &= (-0.0258 \cdot 8) + (0.0040 \cdot 4) + (-8.93) \\ &= -0.206 + 0.016 - 8.93 \\ &= \underline{-9.12} \end{aligned}$$

$$\begin{aligned} \log [Pb]_{\text{free(crit)}} &= (-0.0546 \cdot 8) + (0.0062 \cdot 4) + (-8.19) \\ &= -0.437 + 0.025 - 8.19 \\ &= \underline{-8.60} \end{aligned}$$

##### Step 2

$$\begin{aligned} \log [Cd]_{\text{SPM (crit)}} &= -6.42 + (0.45 \cdot 6) + (0.64 \cdot 1.30) + (0.58 \cdot -9.12) \\ &= -6.42 + 2.70 + 0.832 - 5.29 = -8.178 \\ [Cd]_{\text{SPM (crit)}} &= 6.64 \cdot 10^{-9} (\text{mol g}^{-1}) \cdot 112 \cdot 10^6 = 7.43 \text{ mg kg}^{-1} \end{aligned}$$

$$\begin{aligned} \log [Pb]_{\text{SPM (crit)}} &= -5.42 + (0.70 \cdot 6) + (0.55 \cdot 1.30) + (0.61 \cdot -8.60) \\ &= -5.42 + 4.20 + 0.715 - 5.25 = -5.755 \\ [Pb]_{\text{SPM (crit)}} &= 1.76 \cdot 10^{-6} (\text{mol g}^{-1}) \cdot 207 \cdot 10^6 = 364 \text{ mg kg}^{-1} \end{aligned}$$

##### Step 3

$$\begin{aligned} \text{HARDNESS} &= (0.23 \cdot 8) + (0.34 \cdot 4) + (-0.14) \\ &= 1.84 + 1.36 - 0.14 = 3.1 \end{aligned}$$

Therefore

$$\begin{aligned} [Cd]_{\text{sw(crit)}} &= 0.16 \text{ } \mu\text{g l}^{-1} \\ [Pb]_{\text{sw(crit)}} &= 5 \text{ } \mu\text{g l}^{-1} \end{aligned}$$

##### Step 4

$$\begin{aligned} [Cd]_{\text{tot, sw(crit)}} &= 0.16 + (50 / 1000) \cdot 7.43 \text{ } \mu\text{g l}^{-1} \\ &= 0.20 \text{ } \mu\text{g l}^{-1} \\ [Pb]_{\text{tot, sw(crit)}} &= 5 + (50 / 1000) \cdot 364 \text{ } \mu\text{g l}^{-1} \\ &= 23 \text{ } \mu\text{g l}^{-1} \end{aligned}$$

## FULL CALCULATION EXAMPLE #2

pH = 8  
DOC = 1 mg l<sup>-1</sup>  
pCO<sub>2</sub> = 10 times atmospheric  
SPM = 10 mg l<sup>-1</sup>  
% OM = 20

Step 1

$$\begin{aligned}\log [Cd]_{\text{free(crit)}} &= (-0.0196 \cdot 1) + (0.0466 \cdot 10) + (-9.18) \\ &= -0.020 + 0.466 - 9.18 \\ &= \underline{-8.73}\end{aligned}$$

$$\begin{aligned}\log [Pb]_{\text{free(crit)}} &= (-0.0641 \cdot 1) + (0.0349 \cdot 10) + (-10.33) \\ &= -0.064 + 0.349 - 10.33 \\ &= \underline{-10.05}\end{aligned}$$

Step 2

$$\begin{aligned}\log [Cd]_{\text{SPM (crit)}} &= -6.42 + (0.45 \cdot 8) + (0.64 \cdot 1.30) + (0.58 \cdot -8.73) \\ &= -6.42 + 3.60 + 0.832 - 5.06 = -7.048 \\ [Cd]_{\text{SPM (crit)}} &= 8.95 \cdot 10^{-8} \text{ mol g}^{-1} \cdot 112 \cdot 10^6 = 10.0 \text{ mg kg}^{-1}\end{aligned}$$

$$\begin{aligned}\log [Pb]_{\text{SPM (crit)}} &= -5.42 + (0.70 \cdot 8) + (0.55 \cdot 1.30) + (0.61 \cdot -10.05) \\ &= -5.42 + 5.60 + 0.715 - 6.13 = -5.235 \\ [Pb]_{\text{SPM (crit)}} &= 5.82 \cdot 10^{-6} \text{ mol g}^{-1} \cdot 207 \cdot 10^6 = 1205 \text{ mg kg}^{-1}\end{aligned}$$

Step 3

$$\begin{aligned}\text{HARDNESS} &= (0.36 \cdot 1) + (38.2 \cdot 10) + (-6.84) \\ &= 0.36 + 382 - 6.84 = 376\end{aligned}$$

Therefore

$$\begin{aligned}[Cd]_{\text{sw(crit)}} &= 0.50 \text{ } \mu\text{g l}^{-1} \\ [Pb]_{\text{sw(crit)}} &= 5 \text{ } \mu\text{g l}^{-1}\end{aligned}$$

Step 4

$$\begin{aligned}[Cd]_{\text{tot, sw(crit)}} &= 0.50 + (10/1000) \cdot 10 \text{ } \mu\text{g l}^{-1} \\ &= 0.60 \text{ } \mu\text{g l}^{-1} \\ [Pb]_{\text{tot, sw(crit)}} &= 5 + (10 / 1000) \cdot 1205 \text{ } \mu\text{g l}^{-1} \\ &= 17 \text{ } \mu\text{g l}^{-1}\end{aligned}$$