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 1, which is however not a complete review of possible effects of these metals.

Indicators of effects on ecosystems listed in Table 1 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 5.5.3.3.1, 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 (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 5.5.3.2.

Table 1: 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[*]	a) **Human health** effects	Cd, *Pb*	Arable land	Metal content in food/*fodder* crops
		Cd, Pb	*Grassland*	*Metal content in gras, animal products (cow, sheep)*
		Cd, Pb, Hg	Arable land, grassland, non-agricultural land	Total metal concentration in soil water below the rooting zone (aiming at ground water protection)
	b) **Ecosystem** functioning	Pb, Cd,	Non-agricultural land, arable land, grassland,	Free metal ion concentration in soil solution in view of effects on soil micro-organisms, plants and invertebrates
		Hg	Forests only	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

*) 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 1 and 2, respectively, of the background document (De Vries et al 2004b).

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 to both human health effects (Hg concentration in fish and other animals that serve as a food source to humans) and ecotoxicological effects, since microbioata 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 separately for comparison purposes, the aim is ultimately to provide maps for at most four critical load per metal 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 solution 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 5 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, 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

3

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).

An overview of used symbols and abbreviations is given below.

Some general abbreviations:

M = a flux of a metal M
[M] = a content (in soil, plants) or a concentration (in a solution) of a metal M
f = a fraction
c = a factor for conversion of units

Symbols	Short explanation	Basic units
CL (M)	Critical Load of a 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_w	weathering rate of a metal	$[g\ ha^{-1}\ a^{-1}]$
$M_{le(crit)}$	critical leaching flux of metal with drainage water	$[g\ ha^{-1}\ a^{-1}]$
$M_{ret(crit)}$	net retention of heavy metal in the aquatic system at critical load	$[g\ ha^{-1}\ a^{-1}]$
$M_{lo(crit)}$	critical lateral outflow of heavy metal from the aquatic system	$[g\ ha^{-1}\ a^{-1}]$
A_l	lake area	[ha]
A_c	catchment area	[ha]
SDW	Soil drainage water (including the components of soil solution + SPM)	-
Y_{ha}	yield of harvestable biomass	$[kg\ dw\ ha^{-1}\ a^{-1}]$
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	$[m\ a^{-1}]$
$Q_{le,z}$	leaching flux of water from the rooting zone	$[m\ a^{-1}]$
Q_{lo}	lateral outflow flux of water from the aquatic system	$[m\ a^{-1}]$
$P\ /E_i\ /\ E_s\ /\ E_t$	symbols for water fluxes (water balance equation): Precipitation/ interception evaporation / soil evaporation / (plant) transpiration, resp.	$[m\ a^{-1}]$
$f_{Mu,zb}$	fraction of metal net uptake within the topsoil	[-]
$f_{Mu,z}$	fraction of metal net uptake within the entire rooting zone	[-]
$f_{Et,\ zb}$	fraction of water uptake by plants within the topsoil	[-]
f_f	fractionation or transfer factor describing the Hg contamination of organic matter in solution relative to that in solids	[-]
c_{le}	conversion factor for units (leaching equation)	$[g\ mg^{-1}\ m^2\ ha^{-1}]$
$[M]_{ha}$	metal content in harvestable biomass	$[mg\ kg^{-1}\ dw]$
$[M]_{re}$	reactive content of a metal in soil	$[mg\ kg^{-1}]$
$[M]_{AR},\ [M]_{HF,}$ $[M]_{EDTA,}\ [M]_{HNO3}$	concentration of a metal in soil, extracted with Aqua Regia, HF, EDTA, HNO_3 respectively.	$[mg\ kg^{-1}]$
$[M]_{ss}$	total metal concentration in the soil solution	$[mg\ m^{-3}]$
$[M]_{ss(crit)}$	critical total metal concentration in the soil solution	$[mg\ m^{-3}]$

Symbols	Short explanation	Basic units
$[M]_{sdw(crit)}$	critical total metal concentration in soil drainage water (dissolved and in suspended particles)	$[mg\ m^{-3}]$
$[M]_{free}$	concentration of free metal ion in soil solution	$[mg\ m^{-3}]$
$[M]_{DIC}$	concentration of metal bound to inorganic complexes	$[mg\ m^{-3}]$
$[M]_{DOM}$	concentration of metal bound to dissolved organic matter	$[mg\ m^{-3}]$
$[M]_{SPM}$	concentration of metal bound to suspended particulate matter	$[mg\ kg^{-1}]$
$[M]_{tot,sw(crit)}$	critical total concentration (dissolved and in suspended particles) of heavy metal in surface water	$[mg\ m^{-3}]$
$[M]_{sw[crit]}$	critical dissolved concentration of a heavy metal in surface water	$[mg\ m^{-3}]$
$[Hg]_{OM(crit)}$	critical limit of Hg, normalised for $[OM]s$	$[mg\ (kg\ OM)^{-1}]$
$[Hg]_{Bio}$	critical Hg concentration in biota, e.g. fish flesh	$[mg\ kg^{-1}\ fw]$
$[Hg]_{Prec}$	critical Hg concentration in precipitation	$[ng\ L^{-1}]$
$TFHg_{Site}$	site-specific transfer function linking fish Hg to atmospheric Hg	$[L\ kg^{-1}\ fw]$
$TFHg_{Bio}$	organism-specific transfer function addressing Hg partitioning within food webs	$[-]$
$[OM]_s$	organic matter content of the soil	$[(kg\ OM)\ kg^{-1}]$ or $[\%]$
$[DOM]_{ss}, [DOC]_{ss}$	concentration of dissolved organic matter (carbon) in soil solution	$[g\ m^{-3}]$ or $[mg\ l^{-1}]$
$[[TOC]_{ss}$	concentration of total organic carbon in surface water	$[g\ m^{-3}]$ or $[mg\ l^{-1}]$
$[SPM]_{ss}$	concentration of suspended particulate matter in soil solution	$(kg\ m^{-3})$
$[SPM]_{sw}$	concentration of suspended particulate matter in surface water	$(kg\ m^{-3})$
pH	pH value in soil solution 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 for 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 solution 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:

$$CL(M) = M_u + M_{le(crit)} \tag{1}$$

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 solution.

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,

6

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 5.5.3.3.2).

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 5.5.3.1.2),

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 (equation 2):

$$M_u = f_{Mu} \cdot Y_{ha} \cdot [M]_{ha} \tag{2}$$

where:

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

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 ha^{-1} a^{-1}),

$[M]_{ha}$ =   metal content of the harvestable parts of the plants (g kg^{-1} dw), including also metals deposited on vegetation surfaces (when the metal content is given in mg kg^{-1} 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 ecosystem 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 it 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 2 can be used for orientation, e.g. the average of a range.

Table 2: 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, $[M]_{ha}$ [mg kg^{-1} dw]		
		Pb	Cd	Hg
Grassland	mixed grassland species	1.0 - 3.0	0.05 - 0.25	0.01-0.1
Arable land	wheat (grains) other cereals (grains) potato sugar beet maize	0.1 0.1 - 0.3 0.73 1.0 3.8	0.08 0.02 - 0.06 0.23 0.25 0.2	0.01 0.01 0.02 0.02 0.04
Coniferous forest	spruce, pine, fir, douglas	0.5- 10 0.1 - 0.2	0.1 - 0.5 0.02 - 0.04	0.01-0.05[**] 0.004/0.008[***]
Deciduous forest	oak, beech, birch, poplar	0.5 - 10[**)]	0.05 – 0.5[**)]	

[**)] Hg in spruce stems ≈ 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. 2003

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 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 topsoil

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

$$M_{le(crit)} = c_{le} \cdot Q_{le} \cdot [M]_{ss(crit)} \tag{3}$$

where:

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

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

$[M]_{ss(crit)}$=   critical total concentration of heavy metal in the soil solution (mg m^{-3}) (derived from critical limits, see 5.5.2.2)

c_{le} =   10 g mg^{-1} m^2 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 ($Q_{le,zb}$) at steady state can be calculated according to:

$$Q_{le,zb} = P - E_i - E_s - f_{Et,zb} \cdot E_t \tag{4a}$$

where:

P   = Precipitation (m a^{-1})

E_i = Interception evaporation (m a^{-1})

E_s = Actual soil evaporation within the topsoil defined as above (m a^{-1})

E_t = Actual plant transpiration (m a^{-1})

$f_{Et,zb}$ = 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:

$$Q_{le,zb} = P_m - f_{E,zb} \cdot (P_m^{-2} + (e^{(0.063 \cdot T_m)} \cdot E_{m,pot})^{-2})^{-1/2} \tag{4b}$$

where:

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

T_m = Annual mean air temperature (°C)

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

$f_{E,zb}$ = Fraction of total annual mean evapotranspiration above zb (–); $f_{E,zb} \approx 0.8$ 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 0.1-0.6 m a^{-1}, but may reach >2 m a^{-1} in coastal mountain regions. The standard parameter uncertainty is on the order of ±0.1 m a^{-1} (i.e. about ±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 Equation 4b, Q_{le} almost never drops below 0.1 m^{-1} in Europe (considering EMEP-50 km grid square means). For equation 4a, 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 concentrations of heavy metals in soil solution

Information on the derivation of critical total concentrations of heavy metals in soil solution, $[M]_{ss(crit)}$, either directly, through transfer functions(plant - soil solution) or through $[M]_{free(crit)}$ is given in the next section (5.5.2.2), with background information on used approaches in the Annexes 1-3. The critical total 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^{2+},

$[M]_{\text{free (crit)}}$, and the metals bound to inorganic complexes such as MOH^+, HCO_3^+, MCl^+, $[M]_{DIC}$, and to dissolved organic matter, $[M]_{DOM}$, according to:

$$[M]_{ss(crit)} = [M]_{free(crit)} + [M]_{DIC} + [M]_{DOM} \cdot [DOM]_{ss} \qquad (5)$$

where:
$[M]_{ss(crit)}$ = critical total metal concentration in soil solution (mg m^{-3})
$[M]_{free(crit)}$ = critical free metal ion concentration in soil solution (mg m^{-3})
$[M]_{DIC}$ = concentration of metal bound to inorganic complexes (mg m^{-3})
$[M]_{DOM}$ = concentration of metal bound to dissolved organic matter (mg.kg^{-1})
$[DOM]_{ss}$ = concentration of dissolved organic matter in soil solution (kg m^{-3})

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

$$[M]_{sdw(crit)} = [M]_{ss(crit)} + [M]_{SPM} \cdot [SPM]_{ss} \qquad (6)$$

where:
$[M]_{sdw(crit)}$ = critical total metal concentration in soil drainage water (mg m^{-3})
$[SPM]_{ss}$ = concentration of suspended particulate matter in soil solution (kg m^{-3})

In the calculations, we suggest the latter fraction to be neglected to get comparable values of critical total concentrations for the different effects pathways (see Section 5.5.2.2.3).. In this manual, the values used, are thus all related to the critical total dissolved metal concentrations, $[M]_{ss(crit)}$, implicitly assuming that the concentration of metals bound to suspended particulate matter is negligible ($[M]_{SPM} = 0$).

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, $[M]_{ss(crit)}$, depend on the target to be protected. These values have to be derived from critical limits (see Table 1):

- 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 concentration of a heavy metal in the soil solution ($[M]_{ss(crit)}$) includes both the free metal ions and the metals bound to dissolved inorganic and organic complexes (Eq. 5). The derivation of the critical total dissolved concentrations to be applied in Eq.3, 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 ≥ 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 (Romkens 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 3. The best estimate of a critical Cd concentration might be the mean of both estimates.

Table 3. 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 mg.kg^{-1} fresh weight (0.12 mg.kg^{-1} dry weight) and in brackets the value when applying the limit of 0.2 mg.kg^{-1} fresh weight (EG No 466/2001).

Relationship	Intercept	a	R^2	se	log $[Cd]_{ss(crit)}$ (mM)	$[Cd]_{ss(crit)}$ mg.m^{-3}
$Cd_{Plant} - Cd_{solution}$[1]	1.05	0.39	0.62	0.25	-5.03 (-4.26)	1.05 (6.16)
$Cd_{solution} - Cd_{plant}$[2]	-3.82	1.57	0.62	0.50	-5.28 (-4.81)	0.59 (1.75)

[1] log(Cd plant) = Int + a*log(Cd soil solution)
[2] log(Cd soil solution) = Int + a*log(Cd plant)

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 "**A**s **L**ow **A**s **R**easonably **A**chievable" (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 appriate (for these arguments see De Vries et al. 2003, De Vries et al. 2004a,b). Table 3 provides the parameters for the transfer functions as well as results based on the critical limit of 0.1 mg.kg^{-1} fresh weight (results for the EU limit of 0.2 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 mg.m^{-3} (or 4 mg.m^{-3}). The most conservative estimate equals approximately 0.6 mg.m^{-3} (or 1.75 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, Equation A1.3).

- followed by a transfer function relating the free ion metal activity in solution to the reactive metal content (Annex 1, Equation A1.4 or Equation 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 5.5.3.3.3).

Please note that the current version of W6S-MTC2 is designed to calculate $M_{(ss)crit}$ 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 6 of the background document (De Vries et al., 2004b).

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 1). 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 μg l^{-1}
Cd: 3 μg l^{-1}
Hg: 1 μg l^{-1}
These values can directly be included as $[M]_{ss(crit)}$ 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 1). 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 $M_{ss(crit)}$ from critical limits for free metal ion concentrations using a chemical speciation model.

13

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 H2O, KCl or CaCl2) were used to estimate soil solution pH (pHss) by application of regressions given in Annex 8 of the background document (De Vries et al 2004b). 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.

In bioavailability of metals do 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 solution (pH_{ss}). The derived critical limit functions were:

$$\log[Cd]_{free(crit)} = -0.32 \cdot pH_{ss} - 6.34 \tag{7}$$

$$\log[Pb]_{free(crit)} = -0.91 \cdot pH_{ss} - 3.80 \tag{8}$$

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 Table 4 and 5. 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 $[SPM]_{ss}= 0$, the value of $[Cd]_{SDW(crit)}$ equals that of $[Cd]_{sscrit}$ (see Eq. 6). For reasons of consistency with the other approaches (see before), in which the critical value refers to $[M]_{ss(crit)}$, it is advocated to apply the results with $[SPM]_{ss}= 0$. Furthermore, there ate high uncertainties in the data on SPM in soil solution. Table 4 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 mg.l^{-1}) is small, but for Pb it can be large (Table 5)..

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 above). In the

following recommendations are provided, which status of soil conditions should be considered, when $M_{ss(crit)}$ is derived from critical limits for free metal ion concentrations, as presented in the tables above.

Table 4: Look-up table to derive values of the total critical Cd concentrations in soil drainage water $[Cd]_{SDW(crit)}$ at a CO_2 pressure that equals 15 times the CO_2 pressure of the air

OM	SPM	DOC	$[Cd]_{SDW(crit)}$ (mg.m^{-3}) , being $[Cd]_{ss(crit)}$ (mg.m^{-3}) at SPM=0									
			pH	pH	pH	pH	pH	pH	pH	pH	pH	pH
%dw	mg.l^{-1}	mg.l^{-1}	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	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

Table 5: Look-up table to derive values of the total critical Pb concentrations in soil drainage water $[Pb]_{SDW(crit)}$ at a CO_2 pressure that equals 15 times the CO_2 pressure of the air

OM	SPM	DOC	$[Pb]_{SDW(crit)}$ (mg.m^{-3}) , being $[Pbd]_{ss(crit)}$ (mg.m^{-3}) at SPM=0									
			pH	pH	pH	pH	pH	pH	pH	pH	pH	pH
%dw	mg.l^{-1}	mg.l^{-1}	3.5	4.0	4.5	5.0	5.5	6.0	6.5	7.0	7.5	8.0
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 Gothenborg 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 6, assuming no effect of soil type on the 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.

Table 6 Results of linear regression analyses of the pH in soil solution against pH-H_2O, pH-$CaCl_2$ and pH-KCl

Explaining variable	N	Slope (α)[1]	Intercept (β)[1]	se $_{Yest}$	R_2adj
pH-H_2O	1145	1.0462	-0.2847	0.453	0.84
pH-KCl	905	0.9692	0.6233	0.491	0.80
pH-$CaCl_2$	413	0.8834	1.317	0.741	0.49

1) All coefficients are significant at p > 0,999

More detailed information is given in Annex 8 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 = DOC/50%). 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 9 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 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 9):

Forest organic layer (O horizon): $[DOC]_{ss}$ = 35 mg L^{-1} ($[DOM]_{ss}$ = 70 mg L^{-1}).

Forest mineral topsoil (0-10 cm): $[DOC]_{ss}$ = 20 mg L^{-1} ($[DOM]_{ss}$ = 40 mg L^{-1}).

Grass land (0-10) cm: $[DOC]_{ss}$ = 15 mg L^{-1} ($[DOM]_{ss}$ = 30 mg L^{-1}).

Arable land (0-30) cm: $[DOC]_{ss}$ = 10 mg L^{-1} ($[DOM]_{ss}$ = 20 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 mg (kg 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/org 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.1) 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 solution ($[M]_{ss(crit)}$ in Eq.3, mg m^{-3}) as follows:

$$[Hg]_{ss(crit)} = [Hg]_{SOM(crit)} \cdot f_f \cdot [DOM]_{ss} \cdot c_{ss} \tag{9}$$

where

$[Hg]_{ss(crit)}$ = critical total Hg concentration in soil solution (mg m^{-3})

$[Hg]_{SOM(crit)}$ = critical limit for Hg concentration in solid organic matter (SOM), or the Hg/OM ratio in organic (top)soils ($[Hg]_{SOM(crit)} = 0.5$ mg (kg OM)$^{-1}$).

f_f = fractionation ratio, describing the Hg contamination of organic matter in solution (DOM) relative to that in solids (SOM) (–),

$[DOM]_{ss}$ = concentration of dissolved organic matter in soil solution (g m^{-3}),

c_{ss} = 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 SOM (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 SOM, 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 solution: 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 solution is 35 ng l^{-1} or 0.035 ug.l^{-1} (see Eq. 9). 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 (see De Vries et al. 1998):

$$CL(M) = M_u + M_{ret(crit)} \cdot A_l \: / \: A_c + M_{lo(crit)} \tag{10}$$

where:

$M_{ret(crit)}$ = net retention of heavy metal in the lake at critical load (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:

$$CL(M) = M_u + M_{lo(crit)} \tag{11}$$

where:

M_u = removal of heavy metal by biomass harvesting or net uptake in
                  the catchment (g ha^{-1}a^{-1})
$M_{lo(crit)}$ = critical lateral outflow of heavy metal from the aquatic system (g ha^{-1}a^{-1})

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 term 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. 2), 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.(2) 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:

$$M_{lo(crit)} = 10 \cdot Q_{lo} \cdot [M]_{tot,sw(crit)} \qquad (12)$$

where:
Q_{lo} = lateral outflow flux of water from the aquatic system (m 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 lake area (m^2). The total concentration of metals can be calculated as:

$$[M]_{tot,sw(crit)} = [M]_{sw(crit)} + [M]_{SPM(crit)} \cdot [SPM]_{sw} \qquad (13)$$

where:
$[M]_{sw(crit)}$ = critical dissolved concentration of a heavy metal in surface water (mg m^{-3})
$[M]_{SPM(crit)}$ = 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 4 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 5.5.3.3 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 (mg.m^{-3}). A summary of preliminary effect-based critical limits is given in Table 7. 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 and on Crommentuijn et al. (1997) for the value to be used now, 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 reasons of needing an update of Annex 3 is described below. 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.

Table 7:   Recommended critical limits for dissolved Cd and Pb concentrations surface waters

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

[1] A comparable critical limit is suggested in the RAR on Cd for the protection of top predators, namely 0.26 mg.m^{-3}. This value is based on a critical limit for the intake of Cd of 160 µg 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
[2] H = hardness in mg CaCO3.l^{-1}

The value of 0.38 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 contains and 9 multi-species studies. An assessment factor of 2 is further introduced in the report, leading to a critical limit of 0.19 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 mg CaCO3.l^{-1}) according to 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, using no assessment factor (see also the background document to the manual).

For Pb, the critical limit of 11 mg m^{-3} is based on Crommentuijn et al. (1997), whereas the value of 5 mg m^{-3} (range of 2.1- 9.3 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) 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^{-3} was suggested in dependence on water chemistry, with low values referring to clear softwaters. The critical limit of 5 mg m^{-3} 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 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^{-1}). 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^{-3} (90 percentile range of 0.056- 0.281 mg m^{-3}). 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^{-3} 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]$_{SPM,tot}$) 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-3 for Cd and 11 mg.m-3 for Pb. Use of different values (for Cd as a function of hardiness and for Pb 5 instead of 11 implies a rerun of the WHAM model. This will be done soon and these values can be used, as soon as the updated Annex 3 is available, being foreseen within 2 weeks.

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 Scandianavian 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 form 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:

$$[Hg]_{Pike} = [Hg]_{Prec} \cdot TF_{HgSite} \tag{14}$$

where:
$[Hg]_{Pike}$ = Hg concentration in the flesh of 1-kg pike (ng kg^{-1} fw = 10^6 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

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

$$[Hg]_{PrecCrit} = [Hg]_{PikeCrit} / TF_{HgSite} \tag{15}$$

where:
$[Hg]_{PikeCrit}$ = critical Hg concentration in the flesh of 1-kg pike (0.3 mg kg^{-1} fw)
$[Hg]_{PrecCrit}$ = critical Hg concentration in precipitation (ng L^{-1})

Regarding the critical limit for mercury in pike of 0.3 mg kg^{-1} fw, we refer to the background 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, TFHgSite 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:

$$TF_{HgSite} \approx TF_{HgRun} \cdot ([TOC]_{sw}+1) / ([TP]_{sw}+15) / 0.4 \tag{16a}$$

$$TF_{HgSite} \approx TF_{HgRun} \cdot e^{-(pH-6)/2} \tag{16b}$$

where

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

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

pH   = pH in surface water,

TF_{HgRun} = transfer function (L kg^{-1} 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. Referring to the standard fish (1 kg, in particular pike, *Esox lucius*), TF_{HgRun} has a value around 250 000 L kg^{-1} fw at steady state (Meili et al. 2003a, cf. Verta et al. 1986, Meili 1991a).

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:

$$[Hg]_{Bio} = [Hg]_{Pike} \cdot TF_{HgBio} \quad\quad\quad\quad\quad\quad (17)$$

where:

$[Hg]_{Bio}$ = Hg concentration in any biota, e.g. fish flesh (ng kg^{-1} fw = 10^6 mg kg^{-1} fw)

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

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:

$$TF_{HgBio} \approx f_{HgY} + f_{HgW} \, W^{2/3} \quad\quad\quad\quad\quad\quad (18)$$

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 8)
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 8 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 8).

$$W \approx f_{LW} \cdot L^{3.1} \tag{19}$$

where:

L   = length of the fish (cm)

Table 8:   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	*Esox lucius*	Esocidae	$3.8\ 10^{-6}$	0.87	1.0	1
pike-perch, zander	*Stizostedion lucioperca*	Percidae	$6.4\ 10^{-6}$	1.2	1.0	1.3
perch	*Perca fluviatilis*	Percidae	$7.9\ 10^{-6}$	1.9	0.3	1.0
trout	*Salmo trutta*	Salmonidae	$7.2\ 10^{-6}$	0.4	0.3	0.3
Arctic char	*Salvelinus alpinus*	Salmonidae	$6.8\ 10^{-6}$	0.7	0.3	0.4
whitefish	*Coregonus spp.*	Coregonidae	$6\ 10^{-6}$	<0.4...>2		
burbot	*Lota lota*	Lotidae	$5\ 10^{-6}$	0.9	0.3	0.5
bream	*Abramis brama*	Cyprinidae	$8\ 10^{-6}$	0.25	0.3	0.2
roach	*Rutilus rutilus*	Cyprinidae	$6.8\ 10^{-6}$	0.6...1.2		

Table 8 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 $TF_{HgBio} = 1$.

An important aspect to consider when quantifying steady state parameter values from field data is that present environmental Hg concentrations are not in steady state with the present level of pollution. The approach used here to quantify the future steady state from present survey data is provided in the background document (de Vries et al., 2004).

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 considered here;

- The vertical flux of metals bound to particulate matter suspended in the drainage water, which is not considered in the calculation, may be remarkable in certain soils, this holds in particular for Pb.

- 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

Necessity of transfer functions in deriving critical limits and critical total 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 $M_{(ss)crit}$ can be obtained directly, either by reference to the look up tables or by use of the W6S-MTC2 program (see Section 5.5.3.3.3). In case of ground water protection, total dissolved critical concentrations can be used directly (see Section 5.5.3.3.2). 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 3).

Using the more sophisticated and consistent way to derive soil solution concentrations from critical plant contens 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, Equation A1.3).

- followed by a transfer function relating the free ion metal activity in solution to the reactive metal content (Annex 1, Equation A1.4 or Equation 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 form 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:

$$\log_{10}[M]_{AR} = a_0 + a_1 \cdot \log_{10}[M]_{HF} \tag{A1.1}$$

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.

These functions are not provided here, since those calculations are not needed in the present calculation procedure.

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^{-1})	
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^{-1})	
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^{-1}) can be related to the *pseudo-total* concentration extracted with Aqua Regia $[M]_{AR}$ (mol.kg^{-1}) according to:

$$\log[M]_{RE} = \beta_0 + \beta_1 \cdot \log[M]_{AR} + \beta_2 \cdot \log(\%[OM]_s) + \beta_3 \cdot \log(\%[clay]) \tag{A1.3}$$

Regression relations were derived from a Dutch dataset containing 630 soil samples which were both extracted with 0.43 Mol.l^{-1} HNO$_3$ 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.

Table A1.3 Values for the coefficients β0-β3 in the relationship (Eq. A1.3) between relating reactive, (0.43N HNO$_3$), and *pseudo-total* (aqua regia) soil concentrations, of Cd and Pb, based on a Dutch dataset (Römkens et al. 2004).

Metal	β0	β1	β2	β3	R^2	se-yest[1]
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

1) 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 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 (Q-c 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.

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

$$\log[M]_{free} = a + b \cdot \log[OM]_s + c \cdot pH_{ss} + m \cdot \log[M]_{re} \tag{A1.4}$$

$[M]_{free}$	=	the free metal ion concentration (mol.l^{-1})
$[M]_{re}$	=	the reactive metal content in the solid phase (mol.g^{-1})
$[OM]_s$	=	organic matter (%)
pH_{ss}	=	soil solution 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 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	c	m	R^2	se(Y)
		(SOM)	(pH)	$(\log[M]_{re})$		
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:

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

$[M]_{free}$ = the free metal ion concentration (mol l^{-1})
$[M]_{re}$ = the reactive metal content in the solid phase (mol g^{-1})
$[OM]_s$ = organic matter (%), here the organic matter content of the suspended particles
pH_{ss} = soil solution pH, here 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	c	m	R^2	se(Y)
		$([OM]_s)$	(pH)	$(\log[M]_{free})$		
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

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

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 ($[M]_{free}$, $[M]_{DIC}$, and $[M]_{DOM}$), but also includes $[M]_{SPM}$. 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 given in Annex 1. 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 ($[DOC]_{ss}$) 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$_2$	DOC	SPM

code	the user's identifier of the site
pH	soil solution pH
% OM	the soil organic matter content
pCO$_2$	the soil pCO$_2$ expressed as a multiple of the atmospheric value
DOC	concentration of dissolved organic carbon in mg L^{-1}
SPM	concentration of suspended particulate matter in mg L^{-1}.

- Please see the background document (Annex 8 and 9) regarding the selection of pH and pCO_2 values. If data on DOC concentration are not available, a standard value of 20 mg.l^{-1} will be assumed.

- If data on pCO_2 are not available, a value of 15 × 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, CaCl2, H2O) 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 the critical total aqueous concentration from the critical dissolved concentration using the WHAM model

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.
2. Calculate the metal bound per unit mass of SPM.
3. Sum the total dissolved and particulate concentrations.

Step 1

The free ion concentrations 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). In the calculations the critical dissolved concentrations used were 0.38 $mg.m^{-3}$ for Cd and 11 $mg.m^{-3}$ 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).

The free ion activities calculated with WHAM6 can be expressed in terms of multiple regression equations at different pH values. Thus;

$$\log [M^{2+}] = A \log_{10}[DOC] + B \log_{10} pCO_2 + C \qquad\qquad (A3.1)$$

where [DOC] is in mg L^{-1} and pCO_2 is a multiple of the atmospheric pCO_2. 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 free Cd^{2+} concentrations

pH	A	B	C
4	-0.006	-0.0001	-8.50
5	-0.075	-0.0006	-8.48
6	-0.402	0.0396	-8.49
7	-0.559	0.2171	-8.62
8	-0.304	-0.0881	-8.74
9	-0.014	-0.7092	-9.52

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

pH	A	B	C
4	-0.028	0.0000	-7.31
5	-0.339	0.0004	-7.29
6	-0.869	0.0591	-7.68
7	-1.113	0.2572	-8.77
8	-1.040	0.3491	-9.78
9	-0.222	-1.2027	-11.00

Step 2

The critical SPM–bound metal ($[M]_{SPM (crit)}$, mol g^{-1}) is calculated using the c-Q relations derived in Annex 1, Eq A1.3 (Table A1.4). Before proceeding to Step 3 $[M]_{SPM (crit)}$ must be converted to units of mg kg^{-1}:

$$[Cd]_{SPM(crit)} \text{ (mg kg}^{-1}) = [Cd]_{SPM(crit)} \text{ (mol g}^{-1}) \times (1.124 \times 10^8) \quad\quad (A3.2a)$$

$$[Pb]_{SPM(crit)} \text{ (mg kg}^{-1}) = [Pb]_{SPM(crit)} \text{ (mol g}^{-1}) \times (2.072 \times 10^8) \quad\quad (A3.2b)$$

Step 3

The total aqueous metal at the critical limit is given by:

$$[M]_{tot,\ sw(crit)} = [M]_{sw(crit)} + [M]_{SPM\ (crit)} \times [SPM]_{sw} \quad\quad (A3.3)$$

where $[M]_{sw(crit)}$ is the critical dissolved concentration (mg m^{-3} or µg l^{-1})(Table 10), $[M]_{SPM(crit)}$ is the critical concentration bound to SPM calculated in Step 2 (mg kg^{-1}), and $[SPM]_{sw}$ is the concentration of SPM in the surface water (kg m^{-3} or g l^{-1}).

Calculation examples

For a water of pH 6 with [DOC] = 8 mg l^{-1} a pCO$_2$ four times the atmospheric value and $[SPM]_{sw}$ = 0.050 g l^{-1} (50 mg l^{-1}) with 20% organic matter content:

$$[Cd]_{tot,\ sw(crit)} = 0.38 \text{ µg l}^{-1} + 0.057 \text{ µg l}^{-1} = 0.44 \text{ µg l}^{-1} \quad\quad (A3.4)$$

and

$$[Pb]_{tot,\ sw(crit)} = 11 \text{ µg l}^{-1} + 23.7 \text{ µg l}^{-1} = 33.7 \text{ µg l}^{-1} \quad\quad (A3.5)$$

using the critical limits listed in Table 7 for the critical limits to be used now.

An update of this annex will be made soon by applying critical Cd limits as a function of water hardiness and applying a critical Pb limit of 5 mg.m^{-3}.