V. MAPPING CRITICAL LOADS ON ECOSYSTEMS

Updated by Anne Christine Le Gall, Chairwoman of the Task Force on Modelling and Mapping, from initial text edited by D. Fowler and R. Smith, Mapping Manual 2004
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V.1 INTRODUCTION

The basic idea of the critical load concept is to balance the depositions which an ecosystem is exposed to with the capacity of this ecosystem to buffer the input (e.g., the acidity input buffered by the weathering rate), or to remove it from the system (e.g., nitrogen by harvest) without harmful effects within or outside the system.

The general definition of a critical load (cf chapter I) applies to different receptors (e.g., terrestrial ecosystems, groundwater, aquatic ecosystems, and/or human health). ‘Sensitive elements’ can be part or whole of an ecosystem or of ecosystem development processes, such as their structure and function. Critical loads have been defined for several pollutants and effects resulting from their deposition.

In 1988, critical loads of sulphur and nitrogen acidity for an ecosystem have been specifically defined at the Skokloster Workshop as (Nilsson and Grennfelt, 1988):

“the highest deposition of acidifying compounds that will not cause chemical changes leading to long-term harmful effects on ecosystem structure and function.”

Both sulphur and nitrogen compounds contribute to the total deposition of acidity. The acidity input has to be considered in this balance regardless whether it is due to S or N depositions. Thus, the ratio between sulphur and nitrogen may vary without change in the acidity load.

In the context of a multi-pollutant multi-effects approach it is desirable to consider all effects simultaneously as far as possible. For eutrophication and acidification, this has been done using so-called critical load functions. These are described in detail in section V.4.

In addition to acidification, inputs of nitrogen may influence the eutrophication and nutrient balances of ecosystems. Thus, following the definition for acidity, the critical load for nitrogen nutrition effects was defined as:

\[ \text{Critical Load for Nitrogen Nutrition Effects} = \text{the highest deposition of nitrogen as } \text{NH}_x \text{ and/or NO}_y \text{ below which harmful effects in ecosystem structure and function do not occur according to present knowledge.} \]

Critical loads for heavy metals are defined accordingly.

Critical loads can be established through field observations (empirical critical loads), or computed by means of modelling (computed critical loads). For the latter, either steady-state methods or dynamic models with varying degree of complexity dynamic models with varying degree of complexity can be applied. Empirical critical loads are based on observations of ecological status of ecosystems compared to (measured or modelled) pollutant depositions. Since critical loads are steady-state quantities, the use of dynamic models for the sole purpose of deriving critical loads is somewhat inadequate. However, if dynamic models are used to simulate the transition to a steady state for the comparison with critical loads, care has to be taken that the steady-state version of the dynamic model is compatible with the critical load model. Depending on data availability, assessment of air pollutant impacts may be carried out by one, two or three of these approaches.

This chapter compiles up to date descriptions of the methods to assess empirical and steady state critical loads for eutrophication and acidification. It also describes how to calculate critical loads for heavy metals. Dynamic models are dealt with in a separate chapter (Chapter VI).

\[ \text{Critical Load for Heavy Metals} = \text{the highest deposition of heavy metals that will not cause chemical changes leading to long-term harmful effects on ecosystem structure and function.} \]

---

\[ \text{NH}_x = \text{NH}_3 + \text{NH}_4^+; \quad \text{NO}_y = \text{NO} + \text{NO}_2 + \text{NO}_2^- + \text{NO}_3^- \]


V.2 EMPIRICAL CRITICAL LOADS

Empirical critical loads are based on field observations and experiments (i.e. empirical evidence) that allow to link pollutant deposition to one or several effects on ecosystem parts or functions. These observations may be carried out on experimental sites (with addition or protection from pollutants), on sites submitted to gradients of pollutant deposition (from clean areas to polluted ones, for instance while approaching a source) or on sites that are studied over a long period of time during which deposition levels are known to have increased or decreased.

V.2.1 EMPIRICAL CRITICAL LOADS FOR NUTRIENT NITROGEN

V.2.1.1 THROUGH MANY COMPLEX PROCESSES, NITROGEN HAS SHORT AND LONG TERMS IMPACTS ON ECOSYSTEMS

The emissions of ammonia (NH₃) and nitrogen oxides (NOₓ) have strongly increased in Europe in the second half of the 20th century. This is in relation with the important uses of nitrogen, especially in agriculture, and in relation with emissions from various industrial processes (energy, transport...). Because of short- and long-range transport of nitrogenous compounds, atmospheric nitrogen (nitrogen) deposition has clearly increased in many natural and semi-natural ecosystems.

The availability of nutrients is one of the most important abiotic factors, which determine the plant species composition in ecosystems. Nitrogen is the limiting nutrient for plant growth in many natural and semi-natural ecosystems, especially in oligotrophic and mesotrophic habitats.

Most of the plant species living under such conditions are adapted to nutrient-poor conditions and can only survive or compete successfully on soils with low nitrogen availability (Bobbink and Hettelingh, 2011). In addition, the nitrogen cycle in ecosystems and between the different compartments in the environment is complex, as is illustrated by the “nitrogen cascade” (Figure V.1, Galloway et al., 2003; Sutton et al., 2011). This cycle is strongly regulated by physical, chemical, biological and microbiological processes. As a result of increased air-borne nitrogen pollutants, many changes may therefore occur in soil-based processes, plant growth and in inter-species relationships in each ecosystem.
Figure V.1: Simplified view of the nitrogen cascade, highlighting the transfer of nitrogen species between the different compartments of the environment and their impacts (blue boxes) (adapted from Sutton et al., 2011).

The series of events which occur when nitrogen inputs increase in an area with originally low background deposition rates is highly complex. Many ecological processes interact and operate at different temporal and spatial scales. As a consequence, high variations in sensitivity to atmospheric nitrogen deposition have been observed amongst different natural or semi-natural ecosystems. Despite this diverse sequence of events, the following main effect “categories” can be recognised:

(a) Direct toxicity of nitrogen gases and aerosols to individual species (see nitrogen critical levels);

(b) Accumulation of nitrogen compounds, resulting in increased nitrogen availability and changes of species composition or relative abundance;

(c) Long-term negative effect of ammonium and ammonia;

(d) Soil-mediated effects of acidification;

(e) Increased susceptibility to secondary stress and disturbance factors such as drought, frost, pathogens or herbivores.

V.2.1.2 Updating and reviewing procedures for empirical critical loads and levels

V.2.1.2.1 Organisation

Under the Convention on Long-range Transboundary Air Pollution (LRTAP), empirical critical loads of nitrogen for natural and semi-natural terrestrial ecosystems and wetland ecosystems were firstly presented in a background document for the 1992 workshop on critical loads held under the UNECE LRTAP Convention at Lökeberg (Sweden) (Bobbink et al. 1992). After detailed discussion before and during the meeting, the proposed values were set at that meeting (Grennfelt and Thörnelöf 1992). Additional information from the period 1992–1995 was evaluated and summarised in an updated background paper (Bobbink et al. 1996) and published as Annex III in the previous version of the Mapping Manual (UBA 1996). The updated nitrogen critical loads were discussed and accepted at an expert meeting held in...
December 1995 in Geneva (Switzerland). They were also used in the Air Quality Guidelines for Europe (2nd edition) of the World Health Organisation (WHO 2000). New insights into, and data on, the impacts of nitrogen deposition on natural and semi-natural ecosystems are made available by continuing research. Therefore, relevant information gathered over the years has been discussed, evaluated and approved by consensus in 2002, at an expert meeting held under the LRTAP Convention in Berne (Switzerland, Achermann and Bobbink, 2003), in 2007 at a CLRTAP workshop on critical loads of nitrogen in low-deposition areas (Stockholm, Sweden) and in 2010 at an expert meeting held under the LRTAP Convention in Noordwijk (The Netherlands, Bobbink and Hettelingh, 2011). Each expert proposition for critical loads and levels are adopted by ICP M&M and WGE.

V.2.1.2.2 PROCEDURE FOLLOWED TO DEFINE EMPIRICAL CRITICAL LOADS AND LEVELS

The procedure followed to update empirical critical loads and levels is an iterative process, as presented on Figure V.2. Initially, in both 1992 and 1996, empirical nitrogen critical loads were evaluated for specific receptor groups of natural and semi-natural ecosystems based on observed changes in the structure and function of ecosystems, reported in a range of publication. For each updating procedure, in 2002, 2007 and 2011, the most recent European publications on the effects of nitrogen in natural and semi-natural ecosystems were reviewed. Peer-reviewed publications, book chapters, nationally published papers and “grey” reports of institutes or organisations, if available by request, were incorporated. Results from field addition experiments and mesocosm studies, from correlative or retrospective field studies, and, in few cases, dynamic ecosystem modelling were relevant in this respect. Draft documents were written by a small team of authors for each relevant ecosystem (identified since 2007 as a EUNIS (European Nature Information System, http://eunis.eea.europa.eu/) class, see section V.2.1.2.3) and included a table presenting critical loads and levels. Finalised, these documents became background documents for experts meetings. There, the participants discussed, commented and added information and data to both documents and tables. These were finally approved by ICP M&M and WGE at their following annual meeting. All proceedings and details are in Bobbink and Hettelingh, 2011 and references therein.

![Figure V.2: Schematic representation of the critical loads and levels up-dating procedure (adapted from Bobbink and Hettelingh, 2011).](image-url)
V.2.1.2.3 ECOSYSTEM CLASSIFICATION

To facilitate and harmonise the mapping procedure, the receptor groups of natural and semi-natural ecosystems were classified and ordered according to the EUNIS habitat classification for Europe (Davies et al., 2004). For an introduction to the use of the EUNIS classification see Moss, 2008 and the supporting website (http://eunis.eea.europa.eu/). For an introduction of EUNIS classification with respect to empirical nitrogen critical loads (see Hall et al., 2003).

In general, the ecosystems used in the 2011 updating procedure, were classified down to at least level 3 of the EUNIS hierarchy. The EUNIS codes have been included in the critical loads and levels tables. Also, Natura 2000 habitat types were related to EUNIS classification (see Appendix 1 in Bobbink and Hettelingh, 2011) for correspondences between the EUNIS and the Natura 2000 classifications). Special attention has been paid to woodland and forest habitats (class G) in order to differentiate with precision the critical loads for the different forest types.

Finally, one table has been compiled for seven of the main EUNIS habitat class (EUNIS level 1 code between brackets):

- Marine habitats (A)
- Coastal habitats (B)
- Inland surface water habitats (C)
- Mire, bog and fen habitats (D)
- Grassland and tall forb habitats (E)
- Heathland, scrub and tundra habitats (F)
- Woodland and forests habitats (G)

The other habitats (unvegetated or sparsely vegetated habitats, including caves (H), agricultural (I) and urban zones (J)) have little relevance in the context of long range atmospheric pollution for setting critical loads and levels for nitrogen. Consequently, they were not considered.

V.2.1.3 PROCEDURE TO FOLLOW TO ASSESS AND ATTRIBUTE CRITICAL LOADS ON A TERRITORY

It is recommended that the empirical nitrogen critical loads updated in 2011 (Table V.1) are used to update (national) databases of empirical critical loads.

V.2.1.3.1 REQUIRED DATA

High-resolution maps of sensitive ecosystems of high conservation value (Such as, but not exclusively, Special Areas of Conservation in Natura 2000 network, as defined in the EU, or areas of Special Conservation Interest as defined under the Berne Convention), and/or or ecosystems whose functions are to be protected, are needed per country to map nitrogen critical loads for these systems. Countries are advised to identify those receptor ecosystems of high sensitivity within the mentioned EUNIS classification relating to their individual interest. Effort should be directed to produce fine resolution maps of sensitive ecosystems.

V.2.1.3.2 THE EMPIRICAL CRITICAL LOAD VALUES

For each ecosystem identified on the territory, countries are advised to define which empirical critical load listed in Table V.1 is relevant for use. In this table, each critical load is indicated with the effects to which it is associated. This may be useful to parties to link their empirical critical loads assessments and maps to field observations.
Table V.1: Empirical critical loads for nitrogen deposition (kg N/ha/yr) to natural and semi-natural groups of ecosystems classified according EUNIS. Reliability: ## reliable, # quite reliable and (##) expert judgement. The last column provides a selection of effects that can occur when critical loads are exceeded. Changes with respect to 2003 values are indicated in bold (Bobbink and Hettelingh, 2011).

<table>
<thead>
<tr>
<th>Ecosystem type</th>
<th>EUNIS code</th>
<th>2010 Reliability</th>
<th>2010 kg N ha(^{-1}) yr(^{-1})</th>
<th>Indication of exceedance</th>
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<tr>
<td><strong>Marine habitats (A)</strong></td>
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<tr>
<td>Mid-upper salt marshes</td>
<td>A2.53</td>
<td>20-30 (#)</td>
<td>Increase in dominance of graminoids</td>
<td></td>
</tr>
<tr>
<td>Pioneer salt marshes and low-mid salt marshes</td>
<td>A2.54 and A2.55</td>
<td>20-30 (#)</td>
<td>Increase in late-successional species, increase in productivity</td>
<td></td>
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<tr>
<td><strong>Coastal habitats (B)</strong></td>
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<tr>
<td>Shifting coastal dunes</td>
<td>B1.3</td>
<td>10-20 (#)</td>
<td>Biomass increase, increased N leaching</td>
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<tr>
<td>Coastal stable dune grasslands (grey dunes)</td>
<td>B1.4(^a)</td>
<td>8-15 #</td>
<td>Increase in tall graminoids, decrease in prostrate plants, increased N leaching, soil acidification, loss of typical lichen species</td>
<td></td>
</tr>
<tr>
<td>Coastal dune heaths</td>
<td>B1.5</td>
<td>10-20 (#)</td>
<td>Increase in plant production, increased N leaching, accelerated succession</td>
<td></td>
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<tr>
<td>Moist to wet dune slacks</td>
<td>B1.8(^b)</td>
<td>10-20 (#)</td>
<td>Increased biomass tall graminoids</td>
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<td><strong>Inland surface waters (C)</strong></td>
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<td>Soft-water lakes (permanent oligotrophic waters)</td>
<td>C1.1(^c)</td>
<td>3-10 ##</td>
<td>Change in the species composition of macrophyte communities, increased algal productivity and a shift in nutrient limitation of phytoplankton from N to P</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>1(^2) #</td>
<td>In arctic regions: N deposition between 1 and 1.5 kg N ha(^{-1}) yr(^{-1}): shift in phytoplankton community</td>
<td></td>
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<td></td>
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<td>3-5(^2) ##</td>
<td>In alpine and boreal regions:</td>
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<td></td>
<td></td>
<td>- N deposition between 3 and 5 kg N ha(^{-1}) yr(^{-1}): shift in phytoplankton community</td>
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<td></td>
<td></td>
<td>- N deposition less than 5 kg N ha(^{-1}) yr(^{-1}): higher phytoplankton productivity</td>
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<td></td>
<td>5-10(^2) ##</td>
<td>In temperate, boreal regions:</td>
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<td>• N deposition 2-9 kg N ha(^{-1}) yr(^{-1}): phytoplankton community shift</td>
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<td>• N deposition &lt; 5 kg N ha(^{-1}) yr(^{-1}): higher phytoplankton productivity</td>
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<td>• N deposition 2-12 kg N ha(^{-1}) yr(^{-1}): shift of N to P limitation of benthic algae and productivity of benthic algae increases</td>
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\(^{2}\) As updated by De Wit and Lindholm, 2010.
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<tr>
<th>Ecosystem type</th>
<th>EUNIS code</th>
<th>2010 kg N ha⁻¹ yr⁻¹</th>
<th>2010 Reliability</th>
<th>Indication of exceedance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dune slack pools (permanent oligotrophic waters)</td>
<td>C1.16</td>
<td>10-20²</td>
<td>(#)</td>
<td>Increased biomass and rate of succession</td>
</tr>
<tr>
<td>Permanent dystrophic lakes, ponds and pools</td>
<td>C1.4⁴</td>
<td>3-5²</td>
<td>#</td>
<td>In temperate and boreal regions:</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>• N deposition &lt; 5 kg N ha⁻¹ yr⁻¹; Higher phytoplankton productivity, increased algal productivity and a shift in nutrient limitation of phytoplankton from N to P.</td>
</tr>
</tbody>
</table>

**Mires, bogs and fens (D)**

<table>
<thead>
<tr>
<th>Ecosystem type</th>
<th>EUNIS code</th>
<th>2010 kg N ha⁻¹ yr⁻¹</th>
<th>2010 Reliability</th>
<th>Indication of exceedance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raised and blanket bogs</td>
<td>D1⁵</td>
<td>5-10</td>
<td>##</td>
<td>Increase in vascular plants, altered growth and species composition of bryophytes, increased N in peat and peat water</td>
</tr>
<tr>
<td>Valley mires, poor fens and transition mires</td>
<td>D2⁶</td>
<td>10-15</td>
<td>#</td>
<td>Increase in sedges and vascular plants, negative effects on bryophytes</td>
</tr>
<tr>
<td>Rich fens</td>
<td>D4.1⁷</td>
<td>15-30</td>
<td>(#)</td>
<td>Increase in tall graminoids, decrease in bryophytes</td>
</tr>
<tr>
<td>Montane rich fens</td>
<td>D4.2⁷</td>
<td>15-25</td>
<td>(#)</td>
<td>Increase in vascular plants, decrease in bryophytes</td>
</tr>
</tbody>
</table>

**Grasslands and lands dominated by forbs, mosses or lichens (E)**

<table>
<thead>
<tr>
<th>Ecosystem type</th>
<th>EUNIS code</th>
<th>2010 kg N ha⁻¹ yr⁻¹</th>
<th>2010 Reliability</th>
<th>Indication of exceedance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sub-Atlantic semi-dry calcareous grasslands</td>
<td>E1.26</td>
<td>15-25</td>
<td>##</td>
<td>Increase in tall grasses, decline in diversity, increased mineralisation, N leaching, surface acidification</td>
</tr>
<tr>
<td>Mediterranean xeric grasslands</td>
<td>E1.3</td>
<td>15-25</td>
<td>(#)</td>
<td>Increased production, dominance by graminoids</td>
</tr>
<tr>
<td>Non-Mediterranean dry acidic and neutral closed grasslands</td>
<td>E1.7⁸</td>
<td>10-15</td>
<td>##</td>
<td>Increase in graminoids, decline in typical species, decrease in total species richness</td>
</tr>
<tr>
<td>Inland dune pioneer grasslands</td>
<td>E1.9⁴</td>
<td>8-15</td>
<td>(#)</td>
<td>Decrease in lichens, increase in biomass</td>
</tr>
<tr>
<td>Inland dune siliceous grasslands</td>
<td>E1.9⁵</td>
<td>8-15</td>
<td>(#)</td>
<td>Decrease in lichens, increase in biomass, increased succession</td>
</tr>
<tr>
<td>Low- and medium-altitude hay meadows</td>
<td>E2.2</td>
<td>20-30</td>
<td>(#)</td>
<td>Increase in tall grasses, decrease in diversity</td>
</tr>
<tr>
<td>Mountain hay meadows</td>
<td>E2.3</td>
<td>10-20</td>
<td>(#)</td>
<td>Increase in nitrophilous graminoids, changes in diversity</td>
</tr>
</tbody>
</table>

**Moist and wet oligotrophic grasslands**

- **Molinia caerulea meadows** | E3.51 | 15-25 | (#) | Increase in tall graminoids, decreased diversity, decrease in bryophytes |
- **Heath (Juncus) meadows and humid (Nardus stricta) swards** | E3.52 | 10-20 | # | Increase in tall graminoids, decreased diversity, decrease in bryophytes |
### Mapping critical loads on ecosystems

<table>
<thead>
<tr>
<th>Ecosystem type</th>
<th>EUNIS code</th>
<th>2010 kg N ha(^{-1}) yr(^{-1})</th>
<th>2010 Reliability</th>
<th>Indication of exceedance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moss- and lichen-dominated mountain summits</td>
<td>E4.2</td>
<td>5-10</td>
<td>#</td>
<td>Effects on bryophytes or lichens</td>
</tr>
<tr>
<td>Alpine and subalpine acidic grasslands</td>
<td>E4.3</td>
<td>5-10</td>
<td>#</td>
<td>Changes in species composition; increase in plant production</td>
</tr>
<tr>
<td>Alpine and subalpine calcareous grasslands</td>
<td>E4.4</td>
<td>5-10</td>
<td>#</td>
<td>Changes in species composition; increase in plant production</td>
</tr>
</tbody>
</table>

#### Heathland, scrub and tundra (F)

<table>
<thead>
<tr>
<th>Ecosystem type</th>
<th>EUNIS code</th>
<th>2010 kg N ha(^{-1}) yr(^{-1})</th>
<th>2010 Reliability</th>
<th>Indication of exceedance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tundra</td>
<td>F1</td>
<td>3-5</td>
<td>#</td>
<td>Changes in biomass, physiological effects, changes in species composition in bryophyte layer, decrease in lichens</td>
</tr>
<tr>
<td>Arctic, alpine and subalpine scrub habitats</td>
<td>F2</td>
<td>5-15</td>
<td>#</td>
<td>Decline in lichens, bryophytes and evergreen shrubs</td>
</tr>
<tr>
<td>Northern wet heath</td>
<td>F4.11</td>
<td>10-20</td>
<td>#</td>
<td>Decreased heather dominance, decline in lichens and mosses, increased N leaching</td>
</tr>
<tr>
<td>• ‘U’ Calluna-dominated wet heath (Upland moorland)</td>
<td>F4.11e,h</td>
<td>10-20</td>
<td>#</td>
<td>Transition from heather to grass dominance</td>
</tr>
<tr>
<td>• ‘L’ Erica tetralix-dominated wet heath (Lowland)</td>
<td>F4.11e,h</td>
<td>10-20</td>
<td>(#)</td>
<td></td>
</tr>
<tr>
<td>Dry heaths</td>
<td>F4.2e,h</td>
<td>10-20</td>
<td>##</td>
<td>Transition from heather to grass dominance, decline in lichens, changes in plant biochemistry, increased sensitivity to abiotic stress</td>
</tr>
<tr>
<td>Mediterranean scrub</td>
<td>F5</td>
<td>20-30</td>
<td>(#)</td>
<td>Change in plant species richness and community composition</td>
</tr>
</tbody>
</table>

#### Woodland, forest and other wooded land (G)

<table>
<thead>
<tr>
<th>Ecosystem type</th>
<th>EUNIS code</th>
<th>2010 kg N ha(^{-1}) yr(^{-1})</th>
<th>2010 Reliability</th>
<th>Indication of exceedance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fagus woodland</td>
<td>G1.6</td>
<td>10-20</td>
<td>(#)</td>
<td>Changes in ground vegetation and mycorrhiza, nutrient imbalance, changes in soil fauna</td>
</tr>
<tr>
<td>Acidophilous Quercus-dominated woodland</td>
<td>G1.8</td>
<td>10-15</td>
<td>(#)</td>
<td>Decrease in mycorrhiza, loss of epiphytic lichens and bryophytes, changes in ground vegetation</td>
</tr>
<tr>
<td>Mesotrophic and eutrophic Quercus woodland</td>
<td>G1.A</td>
<td>15-20</td>
<td>(#)</td>
<td>Changes in ground vegetation</td>
</tr>
<tr>
<td>Mediterranean evergreen (Quercus) woodland</td>
<td>G2.1i</td>
<td>10-20</td>
<td>(#)</td>
<td>Changes in epiphytic lichens</td>
</tr>
<tr>
<td>Abies and Picea woodland</td>
<td>G3.1</td>
<td>10-15</td>
<td>(#)</td>
<td>Decreased biomass of fine roots, nutrient imbalance, decrease in mycorrhiza, changed soil fauna</td>
</tr>
<tr>
<td>Pinus sylvestris woodland south of the taiga</td>
<td>G3.4</td>
<td>5-15</td>
<td>#</td>
<td>Changes in ground vegetation and mycorrhiza, nutrient imbalances, increased N(_2)O and NO emissions</td>
</tr>
<tr>
<td>Pinus nigra woodland</td>
<td>G3.5</td>
<td>15</td>
<td>(#)</td>
<td>Ammonium accumulation</td>
</tr>
<tr>
<td>Mediterranean Pinus woodland</td>
<td>G3.7</td>
<td>3-15</td>
<td>(#)</td>
<td>Reduction in fine-root biomass, shift in lichen community</td>
</tr>
</tbody>
</table>
### Ecosystem type

<table>
<thead>
<tr>
<th>Ecosystem type</th>
<th>EUNIS code</th>
<th>2010 Reliability</th>
<th>2010 kg N ha(^{-1}) yr(^{-1})</th>
<th>Indication of exceedance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spruce taiga woodland</td>
<td>G3.A(^{1})</td>
<td>5-10</td>
<td>##</td>
<td>Changes in ground vegetation, decrease in mycorrhiza, increase in free-living algae</td>
</tr>
<tr>
<td>Pine taiga woodland</td>
<td>G3.B(^{1})</td>
<td>5-10</td>
<td>#</td>
<td>Changes in ground vegetation and in mycorrhiza, increase occurrence of free-living algae</td>
</tr>
<tr>
<td>Mixed taiga woodland with Betula</td>
<td>G4.2</td>
<td>5-8</td>
<td>(#)</td>
<td>Increased algal cover</td>
</tr>
<tr>
<td>Mixed Abies-Picea Fagus woodland</td>
<td>G4.6(^{k})</td>
<td>10-20</td>
<td>(#)</td>
<td></td>
</tr>
<tr>
<td>Overall</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Broadleaved deciduous woodland</td>
<td>G1(^{l,m})</td>
<td>10-20</td>
<td>##</td>
<td>Changes in soil processes, nutrient imbalance, altered composition mycorrhiza and ground vegetation</td>
</tr>
<tr>
<td>Coniferous woodland</td>
<td>G3(^{l,m})</td>
<td>5-15</td>
<td>##</td>
<td>Changes in soil processes, nutrient imbalance, altered composition mycorrhiza and ground vegetation</td>
</tr>
</tbody>
</table>

a) For acidic dunes, the 8 to 10 kg N ha\(^{-1}\) yr\(^{-1}\) range should be applied, for calcareous dunes this range is 10 to 15 kg ha\(^{-1}\) yr\(^{-1}\).
b) Apply the lower end of the range to habitats with a low base availability; and the higher end of the range to those with high base availability.
c) This critical load should only be applied to oligotrophic waters with low alkalinity with no significant agricultural or other human inputs. Apply the lower end of the range to boreal and alpine lakes, and the higher end of the range to Atlantic soft waters.
d) This critical load should only be applied to waters with low alkalinity with no significant agricultural or other direct human inputs. Apply the lower end of the range to boreal and alpine dystrophic lakes.
e) Apply the high end of the range to areas with high levels of precipitation and the low end of the range to those with low precipitation levels; apply the low end of the range to systems with a low water table, and the high end of the range to those with a high water table. Note that water tables can be modified by management.
f) For EUNIS category D2.1 (valley mires): use the lower end of the range. Then the reliability is (#).
g) For high-latitude systems, apply the lower end of the range.
h) Apply the high end of the range for areas where sod cutting has been practiced; use the lower end of the range for areas under low intensity management.
i) This critical load has been based on one European study in Portugal and evidence from studies in Mediterranean woodlands in California. During the final editing procedure of this report it became clear that the ambient background deposition of N in the Portuguese study had not been taken into account; therefore, the critical load was subsequently adapted to this value.
j) In Achermann and Bobbink (2003)\(^{1}\) presented as overall value for boreal forests.
k) Included in studies that were classified under EUNIS categories G1.6 and G3.1.
l) In Achermann and Bobbink (2003)\(^{1}\) presented as overall value for temperate forests.
m) For application at broad geographical scales.

#### V.2.1.3.3 RANGES AND RELIABILITY

The empirical nitrogen critical loads are expressed as a range for each ecosystem class, because of:

- real intra-ecosystem variation between different regions where an ecosystem has been investigated;
- the intervals between experimental additions of nitrogen;
- uncertainties in presented total atmospheric deposition values, although the latter have been checked by local specialists on atmospheric nitrogen deposition.

The reliability of the presented nitrogen critical load figures is associated to each critical load, as before (Achermann and Bobbink, 2003, Bobbink et al. 1996), as indicated by the symbols:
• **##**: reliable: when a number of published papers of various studies show comparable results;
• **#:** quite reliable: when the results of some studies are comparable;
• (**#**): expert judgement: when no (robust or reliable) empirical data are available for this type of ecosystem. The nitrogen critical load is then based upon expert judgement and knowledge of ecosystems, which are likely to be more or less comparable with this ecosystem.

Additional qualitative information, in comparison to recommendations provided in Achermann and Bobbink, 2003, on how to interpret the agreed ranges of critical loads in specific situations for an ecosystem was assigned to a number of modifying factors. However, short of agreement on how to quantify modifying factors for assessments on broad regional scales, consensus was reached to use the minimum value of the ranges of empirical critical loads in every EUNIS class to enable the comparison of their exceedances between different air pollution abatement scenarios. This approach is an implementation of the precautionary principle. The details of the methodology used to derive values for empirical critical load ranges are given in Bobbink and Hettelingh, 2011 and in the references therein.

### V.2.1.3.4 RESULTS AND INTERPRETATION

In order to increase the robustness of assessment of nitrogen deposition on ecosystems (Hettelingh et al., 2007), it is advised to use both the mass balance (cf. Section V.4) and empirically derived nitrogen critical loads for ecosystems for which data needed for the application of steady state models is available. If the two approaches yield different values, the one with the lowest values should be used until the background for this difference has been clarified. Here again, a precautionary approach is applied.

### V.2.1.4 CONCLUSIONS ABOUT EMPIRICAL CRITICAL LOADS FOR EUTROPHICATION

The text in this section and in the following one is from Bobbink and Hettelingh (2011).

- A workshop on the review and revision of empirical critical loads and dose-response relationships was held under the Convention on Long-range Transboundary Air Pollution, in Noordwijkhout, The Netherlands, from 23 to 25 June 2010. This workshop was organised by the Coordination Centre for Effects (CCE) and supported by the Dutch Ministry of Housing Spatial Planning and the Environment, the Swiss Federal Office for the Environment and the German Federal Environment Agency.
- The workshop had the following objectives:
  a) Review and revise the empirical critical loads of nitrogen for natural and semi-natural ecosystems, set at an expert workshop held in Berne from 11 to 13 November 2002 (see Achermann and Bobbink, 2003), on the basis of additional scientific information available for the period from late 2002 to 2010, as presented in a new and updated background document.
  b) Provide guidance on how to use site-specific, modifying factors to improve the national application of the empirical approach.
  c) Review relationships between exceedances of the empirical critical loads and species diversity on a European scale, together with possible regional applications.
- The following classes according to the EUropean Nature Information System (EUNIS) were addressed: marine habitats (EUNIS class A), coastal habitats (EUNIS class B), inland surface waters (EUNIS class C), mires, bogs and fens (EUNIS class D),
• Statistically and biologically significant outcomes of field addition experiments and mesocosm studies were the basis for the assessment of empirical N critical loads. Only studies which have independent N treatments and realistic N loads and durations (below 100 kg N ha\(^{-1}\) yr\(^{-1}\); more than 1 yr) were used for the updating and refinement of critical load values. In cases where no appropriate N-addition studies were available, gradient and retrospective studies were given a higher weight.

• Studies with higher N additions or shorter experimental periods were only interpreted with respect to the understanding of effects mechanisms, possible N limitation or sensitivity of the system. The methods used in these studies were carefully scrutinised to identify factors related to the experimental design or data analysis, which may constrain their use in assessing critical loads. This includes evaluation of the precision of the estimated values of background deposition at the experimental site.

• Empirical critical loads for levels 2 and 3 of the EUNIS classification were agreed on for a range of deposition values for all EUNIS classes, including forest and woodland habitats (EUNIS class G). New results regarding nitrogen effects in surface waters could be included on the basis of activities presented by the ICP Waters. Novel findings for some Mediterranean species could be adopted as well. The reliability of empirical critical loads was qualitatively established, distinguishing between ‘reliable’, ‘quite reliable’ and ‘expert judgement’, symbolised by ##, # and (#), respectively.

• Empirical critical loads for nitrogen, resulting from the reviewing and revising procedure were agreed by consensus at the Noordwijkerhout workshop. They are presented in Table V.1

• Additional qualitative information, in comparison to recommendations provided in Achermann and Bobbink (2003), on how to interpret the agreed ranges of critical loads in specific situations for an ecosystem was assigned to a number of modifying factors. However, short of agreement on how to quantify modifying factors for assessments on broad regional scales, consensus was reached to use the minimum value of the ranges of empirical critical loads in every EUNIS class to enable the comparison of their exceedances between different air pollution abatement scenarios.

• To assess effects of exceedances on broad regional scales, it was agreed that specific relationships between the nitrogen load and relevant indicators could be considered, provided that results would only be presented to compare the environmental risk of scenarios in relative terms (see chapter 10 in Bobbink and Hettelingh, 2011).
V.2.1.5 RECOMMENDATIONS ABOUT EMPIRICAL CRITICAL LOADS FOR EUTROPHICATION FROM THE NOORDWIJKERHOUT WORKSHOP

- More well-designed experiments at sites with low background deposition are needed for several sensitive EUNIS classes or in regions with many unstudied ecosystems. Particular attention may be focused on steppe grasslands, all Mediterranean vegetation types, wet swamp forests, mires and fens, forest subtypes (EUNIS level 3), coastal habitats, including shallow marine ecosystems. This will allow further progress in defining and improving empirical critical loads in coming years.

- In order to refine current critical loads, long-term (5-10 years) N-addition experiments using high frequency of N-treatments, between 5 and 50 kg N ha\(^{-1}\) yr\(^{-1}\), in regions with low background depositions, or in mesocosms, are useful. It would increase the reliability of the derived critical loads when the lowest treatment level does not exceed the critical load.

- Gradient (survey) studies with respect to atmospheric nitrogen deposition have been reported or recently initiated. More rigorous guidelines should be developed to evaluate new results from such studies, covering the estimation of deposition rates, the quantification of confounding factors and the application of methods for statistical analysis.

Overall, it remains crucial to understand the long-term effects of increased nitrogen deposition on ecosystem processes in a representative range of ecosystems. It is thus very important to quantify the effects of nitrogen loads by manipulation of nitrogen inputs in long-term ecosystem studies in unaffected and affected areas. These data are essential to validate the set of empirical critical loads, but also to develop existing and new robust dynamic ecosystem models and/or multiple correlative species models, which are reliable enough to assess nitrogen impacts on (semi-)natural ecosystems and to predict (natural) recovery rates for nitrogen-affected systems (see section V.6.4).

V.2.2 EMPIRICAL CRITICAL LOADS FOR ACIDITY

Empirical approaches assign an acidity critical load to soils on the basis of soil mineralogy and/or chemistry. For example, at the Critical Loads Workshop at Skokloster (Nilsson and Grennfelt, 1988), soil forming materials were divided into five classes on the basis of the dominant weatherable minerals. A critical load range, rather than a single value, was assigned to each of these classes according to the amount of acidity that could be neutralised by the base cations produced by mineral weathering (Table V.2).

<table>
<thead>
<tr>
<th>Minerals controlling weathering</th>
<th>Critical load range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz, K-feldspar</td>
<td>&lt;200</td>
</tr>
<tr>
<td>Muscovite, Plagioclase, Biotite (&lt;5%)</td>
<td>200–500</td>
</tr>
<tr>
<td>Biotite, Amphibole (&lt;5%)</td>
<td>500–1000</td>
</tr>
<tr>
<td>Pyroxene, Epidote, Olivine (&lt;5%)</td>
<td>1000–2000</td>
</tr>
<tr>
<td>Carbonates</td>
<td>&gt;2000</td>
</tr>
</tbody>
</table>
The classification of soil materials developed at Skokloster (Table V.2) used a relatively small range of primary silicate minerals and carbonates. A larger range of minerals has been classified by Sverdrup and Warfvinge (1988) and Sverdrup et al. (1990). The following mineral classes have been identified:

- **Very fast weathering** minerals include carbonate minerals that have the potential to dissolve very rapidly, in a geological perspective. The group includes calcite, dolomite, magnesite and brucite.

- **Fast weathering** minerals include the silicate minerals with the fastest weathering rate. The group comprises minerals such as anorthite and nepheline, olivine, garnet, jadeite, diopside. A soil with a major content of these minerals would be resistant to soil acidification. Intermediate weathering minerals include enstatite, hypersthene, augite, hornblende, glaucophane, chlorite, biotite, epidote, zoisite.

- **Slow weathering** minerals include albite, oligoclase, labradorite, illite. Soils with a majority of such minerals will be sensitive to soil acidification.

- **Very slow weathering** minerals include K-feldspar, muscovite, mica, montmorillonite, vermiculite. Soils with a majority of these minerals will be sensitive to soil acidification.

- **Inert** minerals are those that dissolve so slowly or provide so little neutralising substance that they may be considered as inert regarding soil acidification. This includes minerals such as quartz, rutile, anatase, kaolinite, gibbsite.

For each of the above mineral classes, weathering rates for soils with different mineral contents have been proposed (Table V.3, Sverdrup et al., 1990).

### Table V.3: Weathering rates (in eq/(ha·m)/yr) for four selected mineral classes of soil material based on a soil depth of one meter – to convert to critical load values multiply by soil thickness in meters.

<table>
<thead>
<tr>
<th>Mineral class</th>
<th>Average soil mineral class content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100%</td>
</tr>
<tr>
<td>Very fast weathering</td>
<td>25000</td>
</tr>
<tr>
<td>Fast weathering</td>
<td>15000</td>
</tr>
<tr>
<td>Intermediate weathering</td>
<td>10000</td>
</tr>
<tr>
<td>Slow weathering</td>
<td>600</td>
</tr>
<tr>
<td>Very slow weathering</td>
<td>300</td>
</tr>
<tr>
<td>Inert</td>
<td>100</td>
</tr>
</tbody>
</table>

In addition, a number of modifying factors (such as precipitation, vegetation, soil drainage…) were identified that would enable the critical load value to be adjusted within the ranges (Table V.4, after Nilsson and Grennfelt, 1988). For example, some factors could make the soil more sensitive to acidification, requiring the critical load to be set at the lower end of the range, while other factors could make the soil less sensitive, setting the critical load at the upper end of the range.
The information shown in Table V.2 to Table V.4 above provide the basis on which empirical acidity critical loads can be assigned to soils. If mineralogical data are available for the units of a soil map, critical loads can be assigned to each unit and a critical loads map produced.

An example of the development of a critical load map at the national scale using empirical approaches is given by Hornung et al. (1995). In the UK, this approach has been used to define acidity critical loads for non-forest ecosystems, by setting a critical load that will protect the soil upon which the habitat depends (Hall et al. 1998, 2003). The critical load is effectively the base cation weathering rate, with the leaching of acid neutralising capacity (ANC) set to zero (see section V.4.2), and can be used in the calculations of the maximum critical loads of sulphur and nitrogen (see section V.4.3).

Other methods of estimating base cation weathering are discussed in Section V.4.2.

## V.3 MOELLING CRITICAL LOADS FOR TERRESTRIAL ECOSYSTEMS

The purpose of a model-based approach to calculating critical loads is to link, via mathematical equations, a chemical criterion (critical limit) with the maximum deposition(s) ‘below which significant harmful effects on specified sensitive elements of the environment do not occur’, i.e. for which the criterion is not violated. In most cases the ‘sensitive element of the environment’ will be of a biological nature (e.g., the vitality of a tree, the species composition of a heather ecosystem) and thus the criterion should be a biological one. However, there is a dearth of simple yet reliable models that adequately describe the whole chain from deposition to biological impact. Therefore, chemical criteria are used instead, and simple chemical models are used to derive critical loads. This simplifies the modelling process somewhat, but shifts the burden to find, or derive, appropriate (soil) chemical criteria (and critical limits) with proven (empirical) relationships to biological effects. The choice of the critical limit is an important step in deriving a critical load, and much of the uncertainty in critical load calculations stems from the uncertainty in the link between (soil) chemistry and biological impact.

In the following we consider only steady-state models, and concentrate on the so-called Simple Mass Balance (SMB) model as the standard model for calculating critical loads for terrestrial ecosystems under the LRTAP Convention (Sverdrup et al. 1990, Sverdrup and De Vries 1994). The SMB model is a single-layer model, i.e., the soil is treated as a single homogeneous compartment. Furthermore, it is assumed that the soil depth is (at least) the depth of the rooting zone, which allows us to neglect the nutrient cycle and to deal with net growth uptake only. Additional simplifying assumptions include:

- all evapotranspiration occurs on the top of the soil profile;
percolation is constant through the soil profile and occurs only vertically;
- physico-chemical constants are assumed uniform throughout the whole soil profile;
- internal fluxes (such as the weathering rates, N immobilisation etc.) are independent of soil chemical conditions (such as pH);

Since the SMB model describes steady-state conditions, it requires long-term averages for input fluxes. Short-term variations – e.g., episodic, seasonal, interannual, due to harvest and as a result of short-term natural perturbations – are not considered, but are assumed to be included in the calculation of the long-term mean. In this context ‘long-term’ is defined as about 100 years, i.e. at least one rotation period for forests. Ecosystem interactions and processes like competition, pests, herbivore influences etc. are not considered in the SMB model. Although the SMB model is formulated for undisturbed (semi-natural) ecosystems, the effects of extensive management, such as grazing and the burning of moor, could be included.

Besides the single-layer SMB model, there exist multi-layer steady-state models for calculating critical loads. Examples are the MACAL model (De Vries 1988) and the widely-used PROFILE model (Warvigne and Sverdrupt 1992), which has at its core a model for calculating weathering rates from total mineral analyses. These models will not be discussed here, and the interested reader is referred to the literature.

In the following sections we will derive the SMB model for critical loads of nutrient nitrogen (eutrophication) and critical loads of acidifying sulphur and nitrogen.

V.3.1 CRITICAL LOADS OF NUTRIENT NITROGEN (EUTROPHICATION)

V.3.1.1 MODEL DERIVATION

The starting point for calculating critical loads of nutrient N with the SMB model is the mass balance of total nitrogen (N) for the soil compartment under consideration (inputs = sinks + outputs):

\[
N_{dep} + N_{fix} = N_{ad} + N_{i} + N_{u} + N_{de}
+ N_{eros} + N_{fire} + N_{vol} + N_{le}
\]

where:
- \(N_{dep}\) = total N deposition
- \(N_{fix}\) = N 'input' by biological fixation
- \(N_{ad}\) = N adsorption
- \(N_{i}\) = long-term net immobilisation of N in soil organic matter
- \(N_{u}\) = net removal of N in harvested vegetation and animals
- \(N_{de}\) = flux of N to the atmosphere due to denitrification
- \(N_{eros}\) = N losses through erosion
- \(N_{fire}\) = N losses in smoke due to (wild or controlled) fires
- \(N_{vol}\) = N losses to the atmosphere via NH\(_3\) volatilisation
- \(N_{le}\) = leaching of N below the root zone

The units used are eq/ha/yr (or mol/ha\(^{-1}\)a\(^{-1}\) in proper SI nomenclature).

The following assumptions lead to a simplification of eq.V.1:
- Nitrogen adsorption, e.g., the adsorption of NH\(_4\) by clay minerals, can temporarily lead to an accumulation of N in the soil, however it is stored/released only when the deposition changes, and can thus be neglected in steady state considerations.
- Nitrogen fixation is negligible in most (forest) ecosystems, except for N-fixing species.
- The loss of N due to fire, erosion and volatilisation is small for most ecosystems in Europe, and therefore neglected in the following discussion. Alternatively, one could replace \(N_{u}\) by \(N_{i} + N_{eros} + N_{fire} + N_{vol} - N_{fix}\) in the subsequent equations.
- The leaching of ammonium (NH\(_4\)) can be neglected in all forest ecosystems due to (preferential) uptake and...
complete nitrification within the root zone (i.e. \( NH_4 = 0, N_\text{le} = NO_3, \text{le} \)).

Under these simplifying assumptions eq.V.1 becomes:

\[
N_{\text{dep}} = N_i + N_u + N_{\text{de}} + N_{\text{tr}}
\]

(V.2)

From this equation a critical load is obtained by defining an acceptable limit to the leaching of N, \( N_{\text{le}}(\text{acc}) \), the choice of this limit depending on the ‘sensitive element of the environment’ to be protected. If an acceptable leaching is inserted into eq.V.2, the deposition of N becomes the critical load of nutrient nitrogen, \( CL_{\text{nut}}(N) \):

\[
CL_{\text{nut}}(N) = N_i + N_u + N_{\text{de}} + N_{\text{le}}(\text{acc})
\]

(V.3)

In deriving the critical load of nutrient N as eq.V.3, it is assumed that the sources and sinks do not depend on the deposition of N. This is unlikely to be the case and thus all quantities should be taken ‘at critical load’. However, to compute, e.g., ‘denitrification at critical load’ one needs to know the critical load, the very quantity one wants to compute. The only clean way to avoid this circular reasoning is to establish a functional relationship between deposition and the sink of N, insert this function into eq.V.2 and solve for the deposition (to obtain the critical load). This has been done for denitrification: In the simplest case denitrification is linearly related to the net input of N (De Vries et al. 1993, 1994):

\[
N_{\text{de}} = \begin{cases} f_{\text{de}} \cdot (N_{\text{dep}} - N_i - N_u) & \text{if } N_{\text{dep}} > N_i + N_u \\ 0 & \text{else} \end{cases}
\]

(V.4)

where \( f_{\text{de}} (0 \leq f_{\text{de}} < 1) \) is the so-called denitrification fraction, a site-specific quantity. This formulation implicitly assumes that immobilisation and uptake are faster processes than denitrification. Inserting this expression for \( N_{\text{de}} \) into eq.V.2 and solving for the deposition leads to the following expression for the critical load of nutrient N:

\[
CL_{\text{nut}}(N) = N_i + N_u + \frac{N_{\text{le}}(\text{acc})}{1 - f_{\text{de}}}
\]

(V.5)

An alternative, non-linear, equation for the deposition-dependence of denitrification has been proposed by Sverdrup and Ineson (1993) based on the Michaelis-Menten reaction mechanism and includes a dependence on soil moisture, pH and temperature. Also in this case \( CL_{\text{nut}}(N) \) can be calculated explicitly, and for details the reader is referred to Posch et al. (1993).

More generally, it would be desirable to have deposition-dependent equations (models) for all N fluxes in the critical load equation. However, these either do not exist or are so involved that no (simple) explicit expression for \( CL_{\text{nut}}(N) \) can be found. Although this does not matter in principle, it would reduce the appeal and widespread use of the critical load concept. Therefore, when calculating critical loads from eq.V.3 or eq.V.5, the N fluxes should be estimated as long-term averages derived from conditions not influenced by elevated anthropogenic N inputs.

### V.3.1.2 THE ACCEPTABLE LEACHING OF NITROGEN

The value set for the acceptable N leaching depends on the ‘harmful effects’ that should be avoided. In general, it is not the N leaching flux itself that is ‘harmful’, but the concentration of N in the leaching flux. The acceptable N leaching (in eq/ha/yr) is calculated as:

\[
N_{\text{le}}(\text{acc}) = Q \cdot [N]_{\text{acc}}
\]

(V.6)

where \([N]_{\text{acc}}\) is the acceptable N concentration (eq/m³) and \( Q \) is the precipitation surplus (in m³/ha/yr). Values for acceptable N concentrations are given in Table V.5 (see De Vries et al. 2007).
Table V.5: Critical (acceptable) N concentrations in soil solution for calculating $CL_{nut}(N)$.

<table>
<thead>
<tr>
<th>Impact</th>
<th>$[M_{acc}]$ (mgN/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vegetation changes (data established in Sweden):(^1)</td>
<td></td>
</tr>
<tr>
<td>Lichens to cranberry (lingonberries)</td>
<td>0.2–0.4</td>
</tr>
<tr>
<td>Cranberry to blueberry</td>
<td>0.4–0.6</td>
</tr>
<tr>
<td>Blueberry to grass</td>
<td>1–2</td>
</tr>
<tr>
<td>Grass to herbs</td>
<td>3–5</td>
</tr>
<tr>
<td>Vegetation changes (data established in The Netherlands):(^1)</td>
<td></td>
</tr>
<tr>
<td>Coniferous forest</td>
<td>2.5–4</td>
</tr>
<tr>
<td>Deciduous forest</td>
<td>3.5–6.5</td>
</tr>
<tr>
<td>Grass lands</td>
<td>3</td>
</tr>
<tr>
<td>Heath lands</td>
<td>3–6</td>
</tr>
<tr>
<td>Other impacts on forests:</td>
<td></td>
</tr>
<tr>
<td>Nutrient imbalances</td>
<td>(0.2–0.4)</td>
</tr>
<tr>
<td>Elevated nitrogen leaching/N saturation</td>
<td>1</td>
</tr>
<tr>
<td>Fine root biomass/root length</td>
<td>1–3</td>
</tr>
<tr>
<td>Sensitivity to frost and fungal diseases</td>
<td>3–5</td>
</tr>
</tbody>
</table>

1 Note that these values should be used with caution, e.g., in areas with high precipitation.

To convert the values in Table 5 to eq/m\(^3\) divide them by 14. In general, the low leaching values from the above table lead to critical loads that are lower than empirical data on vegetation changes (e.g., Bobbink et al. 1998). It is the increase in N availability through enhanced N cycling that triggers changes (Berendse et al. 1987).

V.3.1.3 SOURCES AND DERIVATION OF INPUT DATA

The obvious sources of input data for calculating critical loads are measurements at the site under consideration. However, in many cases these will not be available. A discussion on N sources and sinks can be found in Hornung et al. (1995) and UNECE (1995). Some data sources and default values and procedures to derive them are summarised below.

V.3.1.3.1 NITROGEN IMMOBILISATION

$N_i$ refers to the long-term net immobilisation (accumulation) of N in the root zone, i.e., the continuous build-up of stable C-N-compounds in (forest) soils. In other words, this immobilisation of N should not lead to significant changes in the prevailing C/N ratio. This has to be distinguished from the high amounts of N accumulated in the soils over many years (decades) due to the increased deposition of N, leading to a decrease in the C/N ratio in the topsoil.

Using data from Swedish forest soil plots, Rosén et al. (1992) estimated the annual N immobilisation since the last glaciation at 0.2–0.5 kgN/ha/yr. Considering that the immobilisation of N is probably higher in warmer climates, values of up to 1 kgN/ha/yr could be used for $N_i$ without causing unsustainable accumulation of N in the soil. It should be pointed out, however, that even higher values (closer to present-day immobilisation rates) have been used in critical load calculations. Although studies on the capacity of forests to absorb nitrogen have been carried out (see, e.g., Sogn et al. 1999), there is no consensus yet on long-term sustainable immobilisation rates.
V.3.1.3.2  NITROGEN UPTAKE

The uptake flux \( N_u \) equals the long-term average removal of N from the ecosystem. For unmanaged ecosystems (e.g., national parks) the long-term (steady-state) net uptake is basically zero whereas for managed forests it is the long-term net growth uptake. The harvesting practice is of crucial importance, i.e., whether stems only, stems plus (parts of) branches or stems plus branches plus leaves/needles (whole-tree harvesting) are removed. The uptake of N is then calculated as:

\[
N_u = \frac{N_{\text{removed in harvested biomass (eq/ha)}}}{\text{interval between harvests (rotation period)(yr)}}
\]

The amount of N in the harvested biomass (stems and branches) can be calculated as following: \( \rho \rho \)

\[
N_u = k_{gr} \cdot N_{ct} \cdot (f_{st,ct} \cdot N_{st} + f_{br,ct} \cdot N_{br})
\]

where \( k_{gr} \) is the average annual growth rate (m³/ha/yr), \( \rho_{st} \) is the density of stem wood (kg/m³), \( ctN \) is the N content in stems (subscript st) and branches (subscript br) (eq/kg) and \( f_{br,ct} \) is the branch-to-stem ratio (kg/kg). The contribution of branches should be neglected in case of stem removal.

Values for the density of stem wood of most trees are in the range of 400–500 kg/m³ for conifers and 550–700 kg/m³ for deciduous trees. The branch-to-stem ratio is about 0.15 kg/kg for conifers and 0.20 kg/kg for deciduous trees (Kimmins et al. 1985, De Vries et al. 1990). According to Swedish data (Rosén 1990; see also Reinds et al. 2001) the contents of N in stems are 1 g/kg for conifers and 1.5 g/kg in deciduous trees, whereas in branches of all tree species the N content is 4 g/kg in the south and 2 g/kg in the north. In a recent report Jacobsen et al. (2002) have summarised the results of a large number of studies on that subject, and Table V.6 shows the average element contents in 4 major tree species, both for stems and branches. For N, the values have to be multiplied by 1/14=0.07143 to obtain the N contents in eq/kg.

### Table V.6: Mean (and standard deviation) of the element contents in stems and branches (both incl. bark) of four tree species (Jacobsen et al. 2002; the number of data points ranges from 6 to 32).

<table>
<thead>
<tr>
<th>Tree species</th>
<th>Contents (g/kg) in stems (incl. bark)</th>
<th>Contents (g/kg) in branches (incl. bark)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
<td>Ca</td>
</tr>
<tr>
<td><strong>Oak</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>quercus spp</em></td>
<td>2.10</td>
<td>2.47</td>
</tr>
<tr>
<td></td>
<td>(0.46)</td>
<td>(1.42)</td>
</tr>
<tr>
<td><strong>Beech</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>fagus sylv.</em></td>
<td>1.54</td>
<td>1.80</td>
</tr>
<tr>
<td></td>
<td>(0.25)</td>
<td>(1.12)</td>
</tr>
<tr>
<td><strong>Spruce</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>picea abies</em></td>
<td>1.22</td>
<td>1.41</td>
</tr>
<tr>
<td></td>
<td>(0.49)</td>
<td>(0.40)</td>
</tr>
<tr>
<td><strong>Pine</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>pinus sylv.</em></td>
<td>1.09</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>(0.30)</td>
<td>(0.30)</td>
</tr>
</tbody>
</table>

\(^a\) Note that for Ca data points from calcareous sites are included in the statistics.
Growth rates used should be long-term average values, typical for the site. It has to be noted that recent growth rates are higher due to increased N input. Therefore, it is recommended to use older investigations (yield tables), preferably from before 1960–70. An example of how to use national inventory information to compute forest growth (and critical loads) in Germany can be found in Nagel and Gregor (1999).

V.3.1.3.3 DENITRIFICATION

Dutch and Ineson (1990) reviewed data on rates of denitrification. Typical values of $N_{de}$ for boreal and temperate ecosystems are in the range of 0.1–3.0 kgN/ha/yr (=7.14–214.3 eq/ha/yr), where the higher values apply to wet(ter) soils; rates for well drained soils are generally below 0.5 kgN/ha/yr.

With respect to deposition-dependent denitrification, values for the denitrification fraction $f_{de}$ have been given by De Vries et al. (1993) based on data from Breeuwsma et al. (1991) and Steenvorden (1984): $f_{de}=0.8$ for peat soils, 0.7 for clay soils, 0.5 for sandy soils with gleyic features and $f_{de}=0–0.1$ for sandy soils without gleyic features. Reinds et al. (2001) related the denitrification fraction to the drainage status of the soil according to Table 5-9:

Table V.7: Denitrification fraction $f_{de}$ as a function of the soil drainage (Reinds et al. 2001).

<table>
<thead>
<tr>
<th>Drainage status</th>
<th>Excessive</th>
<th>Good</th>
<th>Moderate</th>
<th>Imperfect</th>
<th>Poor</th>
<th>Very poor</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_{de}$</td>
<td>0</td>
<td>0.1</td>
<td>0.2</td>
<td>0.4</td>
<td>0.7</td>
<td>0.8</td>
</tr>
</tbody>
</table>

V.3.1.3.4 PRECIPITATION SURPLUS

The precipitation surplus $Q$ is the amount of water percolating from the root zone. It is conveniently calculated as the difference between precipitation and actual evapotranspiration and it should be the long-term climatic mean annual value. In many cases evapotranspiration will have to be calculated by a model using basic meteorological input data (precipitation, temperature, radiation etc.). For the basics of modelling evapotranspiration see Monteith and Unsworth (1990) and for an extensive collection of models see Burman and Pochop (1994). Historical time series of meteorological data can be found, e.g., on the website of the Climate Change Research Unit of the University of East Anglia (www.cru.uea.ac.uk/cru/data).
V.3.2 CRITICAL LOADS OF ACIDITY

V.3.2.1 MODEL DERIVATION: THE SIMPLE MASS BALANCE (SMB) MODEL

The starting point for deriving critical loads of acidifying S and N for soils is the charge balance of the ions in the soil leaching flux (De Vries 1991):

\[ H_{le} + Al_{le} + BC_{le} + NH_{4,le} = SO_{4,le} + NO_{3,le} + Cl_{le} + HCO_{3,le} + RCOO_{le} \]

where the subscript \( le \) stands for leaching, \( Al \) stands for the sum of all positively charged aluminium species, \( BC \) is the sum of base cations (\( BC=Ca+Mg+K+Na \)) and \( RCOO \) is the sum of organic anions. A leaching term is given by \( X_{le}=Q[X] \), where \([X]\) is the soil solution concentration of ion \( X \) and \( Q \) is the precipitation surplus. All fluxes are expressed in equivalents (moles of charge) per unit area and time (eq/ha/yr). The concentrations of \( OH \) and \( CO_3 \) are assumed zero, which is a reasonable assumption even for calcareous soils. The leaching of Acid Neutralising Capacity (ANC) is defined as:

\[ ANC_{le} = HCO_{3,le} + RCOO_{le} - H_{le} - Al_{le} \]

Combination with eq.V.9 yields:

\[ BC_{le} + NH_{4,le} - SO_{4,le} - NO_{3,le} - Cl_{le} = ANC_{le} \]

This shows the alternative definition of ANC as ‘sum of (base) cations minus strong acid anions’. For more detailed discussions on the processes and concepts of (soil) chemistry encountered in the context of acidification see, e.g., the books by Reuss and Johnson (1986) or Ulrich and Sumner (1991).

Chloride is assumed to be a tracer, i.e., there are no sources or sinks of Cl within the soil compartment, and chloride leaching is therefore equal to the Cl deposition (subscript \( dep \)):

\[ Cl_{le} = Cl_{dep} \]

In a steady-state situation the leaching of base cations has to be balanced by the net input of base cations. Consequently the following equation holds:

\[ BC_{le} = BC_{dep} + BC_w - BC_u \]

where the subscripts \( w \) and \( u \) stand for weathering and net growth uptake, i.e. the net uptake by vegetation that is needed for long-term average growth. \( BC=Ca+Mg+K \), reflecting the fact that Na is not taken up by vegetation. Base cation input by litterfall and Bc removal by maintenance uptake (needed to re-supply base cations in leaves) is not considered here, assuming that both fluxes are equal (in a steady-state situation). Also the finite pool of base cations at the exchange sites (cation exchange capacity, CEC) is not considered. Although CEC might buffer incoming acidity for decades, its influence is only a temporary phenomenon, which cannot be taken into account when considering long-term steady-state conditions.

The leaching of sulphate and nitrate can be linked to the deposition of these compounds by means of mass balances for S and N. For S this reads (De Vries 1991):

\[ S_{le} = S_{dep} - S_{ad} - S_{i} - S_{u} - S_{re} - S_{pr} \]

where the subscripts \( ad \), \( i \), \( re \) and \( pr \) refer to adsorption, immobilisation, reduction and precipitation, respectively. An overview of sulphur cycling in forests by Johnson (1984) suggests that uptake, immobilisation and reduction of S is generally insignificant. Adsorption (and in some cases precipitation with Al complexes) can temporarily lead to a strong accumulation of sulphate (Johnson et al. 1979, 1982). However, sulphate is only stored or released at the adsorption complex when the input (deposition) changes, since the adsorbed S is assumed in equilibrium with the soil solution S. Only dynamic models can describe the time pattern of adsorption and desorption of sulphate, but under steady-state conditions S ad- and desorption are not considered. Since sulphur is completely oxidised in the soil profile, \( SO_{4,le} \) equals \( S_{le} \), and consequently:
\[ \text{SO}_{4,\text{le}} = S_{\text{dep}} \] (V.15)

For nitrogen, the mass balance in soil is (see Sec. V.3.1):
\[ N_{\text{le}} = N_{\text{dep}} + N_{\text{fix}} - N_{\text{ad}} - N_i - N_u - N_{\text{de}} - N_{\text{eros}} - N_{\text{vol}} \] (V.16)

where the subscripts fix refers to fixation of N, de to denitrification, and eros, fire and vol to the loss of N due to erosion, forest fires and volatilisation, respectively. \( N_i \) is the long-term immobilisation of N in the root zone, and \( N_u \) the net growth uptake (see above). Furthermore, the leaching of \( \text{NH}_4 \) can be neglected in almost all forest ecosystems due to (preferential) uptake and complete nitrification within the root zone, i.e. \( \text{NH}_4_{\text{le}} = 0 \).

Under these various assumptions eq. V.16 simplifies to:
\[ N_{\text{le}} = NO_{3,\text{le}} = N_{\text{dep}} - N_i - N_u - N_{\text{de}} \] (V.17)

Inserting eqs. 5.12, 5.13, 5.15 and 5.17 into eq. 5.11 leads to the following simplified charge balance for the soil compartment:
\[ S_{\text{dep}} + N_{\text{dep}} = BC_{\text{dep}} - Cl_{\text{dep}} + BC_{w} - Bc_{w} + N_i + N_u \] (V.18)

Strictly speaking, we should replace \( NO_{3,\text{le}} \) in the charge balance not by the right-hand side of eq. V.17, but by \( \max(7(N_{\text{dep}} - N_i - N_u - N_{\text{de}}) \), since leaching cannot become negative; and the same holds true for base cations. However, this would lead to unwieldy critical load expressions: therefore we go ahead with eq. V.18, keeping this constraint in mind.

Since the aim of the LRTAP Convention is to reduce anthropogenic emissions of S and N, sea-salt derived sulphate should not be considered in the balance. To retain charge balance, this is achieved by applying a sea-salt correction to sulphate, chloride and base cations, using either Cl or Na as a tracer, whichever can be (safer) assumed to derive from sea-salts only. Denoting sea-salt corrected depositions with an asterisk, one has either \( Cl_{\text{le}} = 0 \) or \( Na_{\text{le}} = 0 \) (and \( Bc_{\text{le}} = Bc_{\text{dep}} \)), respectively. For procedures to compute sea-salt corrected depositions, see Chapter II.

For given values for the sources and sinks of S, N and Bc, eq. V.18 allows the calculation of the leaching of ANC, and thus assessment of the acidification status of the soil. Conversely, critical loads of S, \( CL(S) \), and N, \( CL(N) \), can be computed by defining a critical ANC leaching, \( ANC_{\text{le, crit}} \).

\[ CL(S) + CL(N) = BC_{\text{dep}}^* - Cl_{\text{dep}}^* + BC_{w} - Bc_{w} + N_i + N_u + N_{\text{de}} - ANC_{\text{le, crit}} \] (V.19)

A so-called critical load of potential acidity has earlier been defined (see Sverdrup et al. 1990) as:
\[ CL(Ac_{\text{pot}}) = BC_{w} - Bc_{w} + N_i + N_u + N_{\text{de}} - ANC_{\text{le, crit}} \] (V.20)

with \( Ac_{\text{pot}} = S_{\text{dep}} + N_{\text{dep}} - BC_{\text{dep}}^* + Cl_{\text{dep}}^* \). The term ‘potential’ is used since \( \text{NH}_4 \) is treated as (potential) acid due to the assumed complete nitrification. \( CL(Ac_{\text{pot}}) \) has been defined to have no deposition terms in its definition, since Bc and Cl deposition are not really an ecosystem property and can (and often do) change over time. However, since these depositions are partly of non-anthropogenic origin (e.g., Saharan dust) and since they are not subject to emission reduction negotiations, they are kept in the critical load definition for convenience.

A further distinction has been made earlier (see, e.g., Sverdrup and De Vries 1994) between ‘land use acidity’ \( Bc_{u} - N_i - N_u - N_{\text{de}} \) and ‘soil acidity’ which is used to define a so-called critical load of (actual) acidity as:
\[ CL(A) = BC_{w} - ANC_{\text{le, crit}} \] (V.21)
The reason for making this distinction was to exclude all variables that may change in the long term such as uptake of Bc and N, which are influenced by forest management, and N immobilisation and denitrification, which may change due to changes in the hydrological regime. There are two problems with this reasoning: (a) the remaining terms in eq.V.21 are also liable to change (e.g. ANC leaching depends on precipitation surplus, see below), and (b) uptake and other N processes are a defining part of the ecosystem (vegetation) itself. In other words, \( CL(A) \) may be a critical load of soil acidity, but it is rarely the soil as such that is the ‘sensitive element’ to be protected, but the vegetation growing on that soil! Nevertheless, quantities such as \( CL(A) \) are computed and reported, and they can have a role as useful short-hand notation for the variables involved.

Note that eq.V.19 does not give a unique critical load for S or N. However, nitrogen sinks cannot compensate incoming sulphur acidity, and therefore the maximum critical load for sulphur is given by:

\[
CL_{\text{max}}(S) = BC_{\text{dep}}^S - CI_{\text{dep}}^S + BC_u - BC_{crit} - ANC_{\text{crit}} + CL(A)
\]

as long as N deposition is lower than all the N sinks, termed the minimum critical load of N, i.e. as long as

\[
N_{\text{dep}} \leq CL_{\text{min}}(N) = N_i + N_u + N_{\text{de}}
\]

Finally, the maximum critical load of nitrogen (in the case of zero S deposition) is given by:

\[
CL_{\text{max}}(N) = CL_{\text{min}}(N) + CL_{\text{max}}(S)
\]

The three quantities \( CL_{\text{max}}(S) \), \( CL_{\text{min}}(N) \) and \( CL_{\text{max}}(N) \) define the critical load function (CLF; depicted in Figure V.3a). Every deposition pair \( (N_{\text{dep}}, S_{\text{dep}}) \) lying on the CLF are critical loads of acidifying S and N.

![Figure V.3](image)

Figure V.3: Critical load function (CLF) of sulphur and acidifying nitrogen, defined by the three quantities \( CL_{\text{max}}(S) \), \( CL_{\text{min}}(N) \) and \( CL_{\text{max}}(N) \). (a) with constant denitrification \( N_{\text{de}} \), and thus a 45\(^{\circ}\) slope of the CLF; (b) with deposition-dependent denitrification, resulting in a smaller \( CL_{\text{min}}(N) \) and a flatter slope, depending on \( f_{\text{de}} \). The grey area below the CLF denotes deposition pairs resulting in an ANC leaching greater than ANC_{le,crit} (non-exceedance of critical loads; see Chapter VI).

Deriving critical loads as above assumes that the sources and sinks of N do not depend on the N deposition. This is unlikely to be true; and as in Section V.3.1 we consider also the case of denitrification being linearly related to the net input of N. Substituting eq.V.4 for \( N_{\text{de}} \) into the equations above results in the following expressions for \( CL_{\text{min}}(N) \) and \( CL_{\text{max}}(N) \):

\[
CL_{\text{min}}(N) = N_i + N_u
\]

and

\[
CL_{\text{max}}(N) = CL_{\text{min}}(N) + \frac{CL_{\text{max}}(S)}{1 - f_{\text{de}}}
\]

where \( f_{\text{de}} \) (0\( \leq f_{\text{de}} < 1 \)) is the denitrification fraction; \( CL_{\text{max}}(S) \) remains the same (eq.V.22). An example of a critical load function with \( f_{\text{de}} > 0 \) is shown in Figure V.3b.
V.3.2.2 CHEMICAL CRITERIA AND THE CRITICAL LEACHING OF ACID NEUTRALISING CAPACITY

The leaching of Acid Neutralising Capacity (ANC) is defined in eq.V.10. In the simplest case bicarbonate (HCO$_3$) and organic anions (RCOO) are neglected since they do not contribute significantly at low pH values (but see below). In this case the ANC leaching is given by:

$$\text{ANC}_{le} = -H_{le} - \text{Al}_{le} = -Q \cdot ([H] + [\text{Al}])$$

where $Q$ is the precipitation surplus in m$^3$/ha/yr (see Section V.3.1.3 for data).

It is within the calculation of $\text{ANC}_{le}$ that the critical chemical criterion for effects on the receptor is set. Selecting the most appropriate method of calculating $\text{ANC}_{le}$ is important, since the different methods may result in very different critical loads. If, for the same ecosystem, critical loads are calculated using different criteria, the final critical load is the minimum of all those calculated. The main decision in setting the criterion will depend on whether the receptor considered is more sensitive to unfavourable pH conditions or to the toxic effects of aluminium. $\text{ANC}_{le}$ can then be calculated by either setting a hydrogen ion criterion (i.e., a critical soil solution pH) and calculating the critical aluminium concentration, or vice versa.

The relationship between $[H]$ and $[\text{Al}]$ is described by an (apparent) gibbsite equilibrium:

$$[\text{Al}] = K_{gibb} \cdot [H]^3$$

or

$$[H] = ([\text{Al}] / K_{gibb})^{1/3}$$

where $K_{gibb}$ is the gibbsite equilibrium constant (see below). Eq.V.28 is used to calculate the (critical) Al concentration from a given proton concentration, or vice versa.

Different critical chemical criteria are listed below together with the equations for calculating $\text{ANC}_{le,crit}$. In this context the reader could also consult the minutes of an Expert Workshop on ‘Chemical Criteria and Critical Limits’ (UNECE 2001, Hall et al. 2001).

V.3.2.2.1 ALUMINIUM CRITERIA

Aluminium criteria are generally considered most appropriate for mineral soils with a low organic matter content. Three commonly used criteria are listed below.

(a) Critical aluminium concentration:

Critical limits for Al have been suggested for forest soils, e.g., $[\text{Al}]_{crit}=0.2$ eq/m$^3$. These are especially useful for drinking water (ground water) protection, e.g., the EC drinking water standard for $[\text{Al}]$ of maximally 0.2 mg/L (about 0.02 eq/m$^3$). $\text{ANC}_{le,crit}$ can then be calculated as:

$$\text{ANC}_{le,crit} = -Q \cdot (([\text{Al}]_{crit} / K_{gibb})^{1/3} + [\text{Al}]_{crit})$$

(b) Critical base cation to aluminium ratio:

Most widely used for soils is the connection between soil chemical status and plant response (damage to fine root) via a critical molar ratio of the concentrations of base cations (Bc=Ca+Mg+K) and Al in soil solution, denoted as $(Bc/\text{Al})_{crit}$. Values for a large variety of plant species can be found in Sverdrup and Warfvinge (1993). The most commonly used value is $(Bc/\text{Al})_{crit}=1$, the value for coniferous forests.

The critical Al leaching is calculated from the leaching of Bc (compare eq.V.13):
The factor 1.5 arises from the conversion of mols to equivalents (assuming that K is divalent). Using eqs.V.27 and V.28, this yields for the critical ANC leaching:

\[ \text{ANC}_{le,crit} = -Q^{2/3} \left( 1.5 \cdot \frac{Bc_{dep} + Bc_w - Bc_u}{K_{gibb} \cdot (Bc/Al)_{crit}} \right)^{1/3} - 1.5 \cdot \frac{Bc_{dep} + Bc_w - Bc_u}{(Bc/Al)_{crit}} \]

Note that the expression \( Bc_{eq} = Bc_{dep} + Bc_w - Bc_u \) has to be non-negative. In fact, it has been suggested that it should be above a minimum leaching or, more precisely, there is a minimum concentration of base cations in the leachate, below which they cannot be taken up by vegetation, i.e., \( Bc_{eq} \) is set equal to \( \max(0, Bc_{dep} + Bc_w - Bc_u - Q[Bc]_{min}) \), with \( [Bc]_{min} \) in the order of 0.01eq/m^3.

(c) Critical aluminium mobilisation rate:

Critical ANC leaching can also be calculated using a criterion to prevent the depletion of secondary Al phases and complexes which may cause structural changes in soils and a further pH decline. Aluminium depletion occurs when the acid deposition leads to an Al leaching in excess of the Al produced by the weathering of primary minerals. Thus the critical leaching of Al is given by:

\[ \text{Al}_{le,crit} = \text{Al}_w \]

where \( \text{Al}_w \) is the weathering of Al from primary minerals (eq/ha/yr). The weathering of Al can be related to the Bc weathering via:

\[ \text{Al}_w = p \cdot BC_w \]

where \( p \) is the stoichiometric ratio of Al to BC weathering in primary minerals (eq/eq), with a default value of \( p=2 \) for typical mineralogy of Northern European soils (range: 1.5–3.0). The critical leaching of ANC becomes then:

\[ \text{ANC}_{le,crit} = -Q^{2/3} \left( \frac{p \cdot BC_w}{K_{gibb}} \right)^{1/3} - p \cdot BC_w \]

_A. HYDROGEN ION CRITERIA_

A proton criterion is generally recommended for soils with a high organic matter content. Two such criteria are listed below.

(a) Critical pH:

A critical pH limit is set at a pH below which the receptor is adversely affected. Critical limits have been suggested for forest soils, for example, \( pH_{crit}=4.0 \) (corresponding to \( [H]_{crit}=0.1 \) eq/m^3). ANC_{le,crit} can then be calculated as:

\[ \text{ANC}_{le,crit} = -Q \left( [H]_{crit} + K_{gibb} \cdot [H]^3_{crit} \right) \]

(b) Critical base cation to proton ratio:

For organic soils which do not contain Al-(hydr)oxides (such as peat lands), it is suggested to use a critical molar base cation to proton ratio \( (Bc/H)_{crit} \). The critical ANC leaching is then given by (no Al leaching!):

\[ \text{ANC}_{le,crit} = 0.5 \cdot \frac{Bc_{dep} + Bc_w - Bc_u}{(Bc/H)_{crit}} \]

where the factor 0.5 comes from converting mols to equivalents. For organic soils the weathering in eq.V.36 will probably be negligible \( (Bc_w=0) \). Values suggested for \( (Bc/H)_{crit} \) are expressed as multiples of \( (Bc/Al)_{crit} \), these multiples ranging from 0.3 for deciduous trees and ground vegetation to 1 for spruce and pine (Sverdrup and Warfvinge 1993).
V.3.2.2.3 CRITICAL BASE SATURATION

Base saturation, i.e., the fraction of base cations at the cation exchange complex, is an indicator of the acidity status of a soil, and one may want to keep this pool above a certain level to avoid nutrient deficiencies. Thus a critical (acceptable, minimum) base saturation could be chosen as a criterion for calculating critical loads of acidity (see Hall et al. 2001, UNECE 2001).

To relate base saturation to ANC requires the description of the exchange of cations between the exchange complex and the soil solution. Two descriptions are the most commonly used in dynamic soil models: the Gapon and the Gaines-Thomas exchange model. For a comparison between different exchange models and the implications for the relationship between base saturation and soil solution concentrations see Reuss (1983).

As an example, we consider the description of the exchange between H, Al and Bc=Ca+Mg+K as implemented in the Very Simple Dynamic (VSD) as well as the SAFE model (see Posch et al. 2003a or Chapter VI on dynamic modelling). For both models the critical concentration \([H]_{\text{crit}}\) can be found as a solution of an equation of the type:

\[
A \cdot [H]_{\text{crit}}^p + B \cdot [H]_{\text{crit}} = 1 - E_{Bc,\text{crit}}
\]

where the coefficients \(A\), \(B\) and the exponent \(p\) are given in Table 5-10.

Table V.8: Coefficients in eq.V.37 for the Gapon and Gaines-Thomas exchange model.

<table>
<thead>
<tr>
<th>Exchange model</th>
<th>(A)</th>
<th>(p)</th>
<th>(B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gapon</td>
<td>(K_{Alox}^{1/3} \cdot k_{AlBc} \cdot E_{Bc,\text{crit}} / \sqrt{[Bc]})</td>
<td>(a/3)</td>
<td>(k_{HBC} \cdot E_{Bc,\text{crit}} / \sqrt{[Bc]})</td>
</tr>
<tr>
<td>Gaines-Thomas</td>
<td>(K_{Alox}^{1/3} \cdot k_{AlBc} \cdot (E_{Bc,\text{crit}} / [Bc])^3)</td>
<td>(a)</td>
<td>(K_{HBC}^{1/3} \cdot E_{Bc,\text{crit}} / [Bc])</td>
</tr>
</tbody>
</table>

Note: The generalised relationship \([Al]=K_{Alox}[H]^a\) has been used (see below).

In general, eq.V.37 is non-linear and will have to be solved numerically. Only for the Gapon model and the gibbsite equilibrium (\(a=3\), \(K_{Alox}=K_{gibb}\)) it becomes a linear equation with the solution:

\[
[H]_{\text{crit}} = K_{\text{Gap}} \cdot \sqrt{[Bc]} \cdot \left( \frac{1}{E_{Bc,\text{crit}}} - 1 \right)
\]

with

\[
K_{\text{Gap}} = \frac{1}{k_{HBC} + k_{AlBc} \cdot K_{gibb}^{1/3}}
\]

where \(k_{HBC}\) and \(k_{AlBc}\) are the two (site-specific) selectivity coefficients describing cation exchange and \([Bc]=Bc/Q\) as above. \([Al]_{\text{crit}}\) is then computed from the gibbsite equilibrium (eq.V.28) and from that the critical ANC leaching can be obtained via eq.V.29. Values of selectivity coefficients for a range of (Dutch) soil types and combinations of exchangeable ions are given by De Vries and Posch (2003).

In Figure V.4 the critical ANC leaching is shown for a range of constants \(K_{\text{Gap}}\). This range encompasses a wide range of values for the exchange constants. The figure shows that ANC leaching is very sensitive to low values of the critical base saturation.
Base saturation is also used as criterion in the New England Governors/Eastern Canadian Premiers ‘Acid Rain Action Plan’ for calculating sustainable S and N depositions to upland forests with the SMB model (NEG/ECP 2001).

### V.3.2.3 SOURCES AND DERIVATION OF INPUT DATA

The obvious sources of input data for calculating acidity critical loads are measurements at the site under consideration. However, in many cases these will not be available. For data on the different N quantities see Section V.3.1. Some data sources and default values for the other variables, and procedures to derive them, are summarised below.

#### V.3.2.3.1 GIBBSITE EQUILIBRIUM CONSTANT ($K_{\text{gibb}}$)

The equilibrium constant relating the Al concentration to pH (eq.V.28) depends on the soil. Table V.9 presents ranges of $K_{\text{gibb}}$ (and $pK_{\text{gibb}}=-\log_{10}(K_{\text{gibb}}$ in (mol/L)$^{-2}$) as a function of the soil organic matter content. A widely used default value is

$$K_{\text{gibb}}=10^8 \text{ (mol/L)}^{-2}=300 \text{ m}^6/\text{eq}^2.$$ 

<table>
<thead>
<tr>
<th>Soil type; layer</th>
<th>Organic matter (%)</th>
<th>$K_{\text{gibb}}$ (m$^6$/eq$^2$)</th>
<th>$pK_{\text{gibb}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral soils; C-layer</td>
<td>&lt;5</td>
<td>950–9500</td>
<td>8.5–9.5</td>
</tr>
<tr>
<td>Soils with low organic matter; B/C layers</td>
<td>5–15</td>
<td>300–3000</td>
<td>8–9</td>
</tr>
<tr>
<td>Soils with some organic material; A/E layers</td>
<td>15–30</td>
<td>100</td>
<td>7.6</td>
</tr>
<tr>
<td>Peaty and organic soils; organic layers</td>
<td>&gt;70</td>
<td>9.5</td>
<td>6.5</td>
</tr>
</tbody>
</table>

If sufficient empirical data are available to derive the relationship between [$H$] and [$Al$], these should be used in preference to the gibbsite equilibrium (see Sec. V.3.2.4).
V.3.2.3.2 BASE CATION AND CHLORIDE DEPOSITION

The base cation and chloride depositions entering the critical load calculations should be the deposition after all feasible abatement measures have been taken (ideally the non-anthropogenic deposition), and they should be sea-salt corrected. Observations on a European scale are available from the EMEP Chemical Co-ordinating Centre (www.emep.int) or from national sources. See Chapter II for more details.

V.3.2.3.3 BASE CATION WEATHERING

Weathering here refers to the release of base cations from minerals in the soil matrix due to chemical dissolution, and the neutralisation and production of alkalinity connected to this process. This has to be distinguished from the denudation of base cations from ion exchange complexes (cation exchange) and the degradation of soil organic matter. Many methods for determining weathering rates have been suggested, and here we list those with the highest potential for regional applications (in order of increasing complexity).

(a) The Skokloster assignment

This is a (semi-)empirical method devised at the Critical Loads Workshop at Skokloster (Sweden) (Table 1, p.40 in Nilsson and Grennfelt 1988). Details can be found in the section on empirical acidity critical loads (Section V.2.2).

(b) The soil type - texture approximation

Since mineralogy controls weathering rates, weathering rate classes were assigned to European (forest) soils by De Vries et al. (1993), based on texture class and parent material class. Texture classes are defined in Table V.10 as a function of their clay and sand content:

Table V.10: Soil texture classes as a function of their clay and sand content (Eurosoil 1999).

<table>
<thead>
<tr>
<th>Texture class</th>
<th>Name</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>coarse</td>
<td>clay &lt; 18 % and sand ≥ 65 %</td>
</tr>
<tr>
<td>2</td>
<td>medium</td>
<td>clay &lt; 35% and sand &gt; 15 %,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>but clay ≥ 18 % if sand ≥ 65 %</td>
</tr>
<tr>
<td>3</td>
<td>medium fine</td>
<td>clay &lt; 35% and sand &lt; 15 %</td>
</tr>
<tr>
<td>4</td>
<td>fine</td>
<td>35 % ≤ clay &lt; 60 %</td>
</tr>
<tr>
<td>5</td>
<td>very fine</td>
<td>clay ≥ 60 %</td>
</tr>
</tbody>
</table>

Using the FAO soil classification (FAO 1981), the parent material class has been defined for each soil type in Table V.11 (updated from De Vries et al. 1993).
Table V.11: Parent material classes for common FAO soil types (Posch et al. 2003b).

<table>
<thead>
<tr>
<th>Parent material</th>
<th>FAO soil type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic</td>
<td>Ah, Ao, Ap, B, Ba, Bd, Be, Bf, Bh, Bm, Bx, D, Dd, De, Dg, Gx, I, Id, Ie, Jd, P, Pf, Pg, Ph, Pl, Po, Pp, Q, Qa, Qc, Qh, Ql, Rd, Rx, U, Ud, Wd</td>
</tr>
<tr>
<td>Intermediate</td>
<td>A, Af, Ag, Bv, C, Cg, Ch, Cl, G, Gd, Ge, Gf, Gh, Gi, Gl, Gm, Gs, Gt, H, Hg, Hh, Hl, J, Je, Jm, Jt, L, La, Ld, Lf, Lg, Lh, Lo, Lp, Mo, R, Re, V, Vg, Vp, W, We</td>
</tr>
<tr>
<td>Basic</td>
<td>F, T, Th, Tm, To, Tv</td>
</tr>
<tr>
<td>Organic</td>
<td>O, Od, Oe, Ox</td>
</tr>
</tbody>
</table>

Acidic: Sand(stone), gravel, granite, quartzine, gneiss (schist, shale, greywacke, glacial till)
Intermediate: Giron diorite, loess, fluvial and marine sediments (schist, shale, greywacke, glacial till)
Basic: Gabbro, basalt, dolomite, volcanic deposits.

From texture and parent material class the weathering rate class is obtained from Table V.12 (modified from De Vries et al. 1993).

Table V.12: Weathering rate classes as a function of texture and parent material classes (Posch et al. 2003b).

<table>
<thead>
<tr>
<th>Parent material</th>
<th>Texture class</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Acidic</td>
<td>1</td>
</tr>
<tr>
<td>Intermediate</td>
<td>2</td>
</tr>
<tr>
<td>Basic</td>
<td>2</td>
</tr>
<tr>
<td>Organic</td>
<td>class 6 for Oe and class 1 for other organic soils</td>
</tr>
</tbody>
</table>

The actual weathering rate (in eq/ha/yr) for a non-calcareous soil of depth \(z\) (in m) is then computed as:

\[
BC_w = z \cdot 500 \cdot (WRc - 0.5) \cdot \exp \left( \frac{A}{281} - \frac{A}{273 + T} \right)
\]

where \(WRc\) is the weathering rate class (Table V.12), \(T\) (°C) is the average annual (soil) temperature and \(A=3600\) K (Sverdrup 1990). For calcareous soil, for which critical loads are not really of interest, one could set, e.g., \(WRc=20\) in eq.V.39.

The above procedure provides weathering rates for BC=Ca+Mg+K+Na. However, for computing the critical ANC leaching according to eq.5.31, the weathering rate for Bc=Ca+Mg+K is needed. \(Bc_w\) can be approximated by multiplying \(BC_w\) with a factor between 0.70 for poor sandy soils and 0.85 for rich (sandy) soils. Van der Salm et al. (1998) (for texture classes 2–5, see Table 5-12 and De Vries (1994) (for texture class 1) provide regression equations for weathering rates of Ca, Mg, K and Na as a function of the sand (and silt) content of the soil, which can be used to split \(BC_w\) into individual weathering rates.

(c) The total base cation content correlation

Using the ‘zirconium method’, Olsson et al. (1993) derived from 11 Swedish sites a correlation between the historical average weathering rates of base cations and the total content of the respective element in the undisturbed bottom soil, with an additional temperature correction. For Ca, Mg and K the equations are (Olsson et al. 1993, converted to eq/ha/yr):

\[
Ca_w = 0.13 \cdot (Ca)_{tot} \cdot ETS - 55.5
\]

\[
Mg_w = 0.23 \cdot (Mg)_{tot} \cdot ETS - 24.1
\]

\[
K_w = 0.05 \cdot (K)_{tot} \cdot ETS - 79.8
\]
where \((X)_{\text{tot}}\) is the total content of element \(X\) (in dry weight %) in the coarse fraction (<2mm) of the undisturbed C-horizon soil and ETS is the annual sum of daily temperatures above a threshold of +5°C. Care has to be taken when applying these formulae, since they are based on Nordic geological history, they do not predict the weatherable soil depth, which was found to vary between 20 and 200 cm in the field data, and they don’t cover many soil types (mostly podzols).

Using the part of the Swedish data (7–8 sites depending on the element, covering a weatherable depth of 20–100 cm), this method was adapted in Finland for estimating weathering rates on a national scale (Johansson and Tarvainen 1997, Joki-Heiskala et al. 2003).

(d) The calculation of weathering rates with the PROFILE model

Weathering rates can be computed with the multi-layer steady-state model PROFILE.

V.3.2.3.4 BASE CATION UPTAKE

The uptake flux of base cations, \(B_{\text{cu}}\), entering the critical load calculations is the long-term average removal of base cations from the ecosystem. The uptake fluxes should be calculated for the individual base cations (Ca, Mg and K) separately. The considerations and calculations are exactly the same as for the uptake of N (see Section V.3.1). Average contents of Ca, Mg and K in stems and branches can be found in Table 5-8 (see also Jacobsen et al. 2002). Values have to be multiplied by 2/40.08, 2/24.31 and 1/39.10 for Ca, Mg and K, respectively, to obtain contents in eq/kg.

The (long-term) net uptake of base cations is limited by their availability through deposition and weathering (neglecting the depletion of exchangeable base cations). Furthermore, base cations will not be taken up below a certain concentration in soil solution, or due to other limiting factors, such as a temperature. Thus the values entering critical load calculations should be constrained by:

\[
Y_u \leq Y_{\text{dep}} + Y_w - Q \cdot [Y]_{\min}
\]

(V.41) for

\[
Y = Ca, Mg, K
\]

This is preferable to constraining the sum \(B_{\text{cu}} = Ca_k + Mg_k + K_k\) (see eq.V.31). Suggested values are 5 meq/m\(^3\) for \([Ca]_{\min}\) and \([Mg]_{\min}\), and zero for \([K]_{\min}\) (Warfvinge and Sverdrup 1992). It should also be taken into account that vegetation takes up nutrients in fairly constant (vegetation-specific) ratios. Thus, when adjusting the uptake value for one element, the values for the other elements (including N) should be adjusted proportionally.
V.3.2.4 POSSIBLE EXTENSIONS TO THE SMB MODEL

In the following three suggestions are made for generalising the SMB model, with the idea of improving the critical load calculations but also with the aim to enhance the compatibility with dynamic models. All three suggestions are ‘backwards-compatible’, i.e. by setting key parameters to zero the original SMB model is obtained. For an earlier discussion of these extensions see also Posch (2000).

(a) Generalisation of the Al-H relationship

In the SMB model the relationship between Al concentration and pH is described as gibbsite equilibrium (see eq.V.21). However, Al concentrations, especially in the topsoil, can be influenced by the complexation of Al with organic matter (Cronan et al. 1986, Mulder and Stein 1994). Therefore, the gibbsite equilibrium in the SMB model could be generalised by:

\[ aA_{lox}^aHK_{Al} = \text{constant} \]

with equilibrium constant \( K_{\text{Al}_{\text{ox}}} \) and exponent \( a \). Obviously, the gibbsite equilibrium is a special case of eq.V.42 (setting \( a=3 \) and \( K_{\text{Al}_{\text{ox}}}=K_{\text{gibb}} \)). The exponent \( a \) and \( K_{\text{Al}_{\text{ox}}} \) depend on the soil type and especially on the soil horizon. As an example, in Table V.13 values for \( K_{\text{Al}_{\text{ox}}} \) and \( a \) are presented for different soil groups and soil depths derived from several hundred Dutch forest soil solution samples (see Van der Salm and De Vries 2001).

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Depth (cm)</th>
<th>( \log_{10} K_{\text{Al}_{\text{ox}}} )</th>
<th>( a )</th>
<th>( N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>All</td>
<td>humus layer</td>
<td>-1.03</td>
<td>1.17</td>
<td>275</td>
</tr>
<tr>
<td>Sandy soils</td>
<td>0–10</td>
<td>3.54</td>
<td>2.26</td>
<td>274</td>
</tr>
<tr>
<td></td>
<td>10–30</td>
<td>5.59</td>
<td>2.68</td>
<td>377</td>
</tr>
<tr>
<td></td>
<td>30–100</td>
<td>7.88</td>
<td>3.13</td>
<td>271</td>
</tr>
<tr>
<td>Loess soils</td>
<td>0–10</td>
<td>-0.38</td>
<td>1.04</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>10–30</td>
<td>3.14</td>
<td>1.83</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>30–100</td>
<td>4.97</td>
<td>2.21</td>
<td>40</td>
</tr>
<tr>
<td>Clay</td>
<td>all depths</td>
<td>4.68</td>
<td>2.15</td>
<td>152</td>
</tr>
<tr>
<td>Peat</td>
<td>all depths</td>
<td>1.41</td>
<td>1.85</td>
<td>163</td>
</tr>
</tbody>
</table>

\( a \) and \( K_{\text{Al}_{\text{ox}}} \) values for \( K_{\text{Al}_{\text{ox}}} \) are derived from \([Al] \) and \([H] \) in mol/L; the unit of \( K_{\text{Al}_{\text{ox}}} \) depends on \( a \) and is (mol/L)\(^{-a}\). The data in Table V.13 show that a standard gibbsite equilibrium constant \( a=3 \) is reasonable for (Dutch) sandy soils. Very different values, however, are obtained for peat soils and, to a lesser extent, also for loess and clay soils (especially for shallow parts of the soil, where the organic matter content is highest). Data from intensive forest monitoring plots show that there is a strong correlation between \( a \) and \( \log_{10} K_{\text{Al}_{\text{ox}}} \) (De Vries et al. 2003, p.118), which emphasises that these two parameters cannot be chosen independently.

Figure V.5 shows the relationship between \([H] \) and \([Al] \) as well as its logarithmic form for different values of \( K_{\text{Al}_{\text{ox}}} \) and \( a \). Defining \( pX=-\log_{10}[X] \), with \([X] \) given in mol/L, one has \( \text{pH}=3-\log_{10}(H) \), if \([H] \) is expressed in eq/m\(^3\); and for \([Al] \) in eq/m\(^3\) the relationship is \( \text{pAl}=3-\log_{10}(Al/3) \).
Note that, when using eq.V.42 instead of eq.V.28, the formulae for $ANC_{le,crit}$ have to be adapted as well (mostly replacing the exponent 3 by $a$ and 1/3 by 1/$a$).

(b) Including bicarbonate leaching

The charge balance (eq.V.9) and the definition of ANC leaching in eq.V.10 also includes the leaching of bicarbonate anions ($HCO_3^{-}$, $le=Q[HCO_3^{-}]$). The concentration of bicarbonates is a function of the pH:

\[
[HCO_3^{-}] = \frac{K_1 \cdot KH \cdot p_{CO_2}}{[H]}
\]

where $K_1$ is the first dissociation constant, $KH$ is Henry’s constant and $p_{CO_2}$ is the partial pressure of $CO_2$ in the soil solution (in atm). The two constants are weakly temperature-dependent, and the value for their product at 8°C is $K_1/K_H=10^{-1.7}=0.02$ eq$^2$/m$^3$/atm. For systems open to the atmosphere, $p_{CO_2}$ is about 370 ppm or $3.7 \cdot 10^{-4}$ atm (in the year 2000). However, in soils $p_{CO_2}$ is generally higher (ranging from $10^{-2}$ to $10^{-1}$ atm, Bolt and Bruggenwerf 1976), due to respiration and oxidation of below-ground organic matter. Respiratory production of $CO_2$ is highly temperature dependant (e.g. Witkamp 1966); based on soil temperature and mean growing season soil $p_{CO_2}$, Gunn and Trudgill (1982) derived the following relationship:

\[
\log_{10} p_{CO_2} = -2.38 + 0.031 \cdot T
\]

where $T$ is the (soil) temperature (°C). Brook et al. (1983) present a similar regression equation based on data for 19 regions of the world. In the absence of data or such relationships, the following default ranges have been suggested (Bouten et al., 1987): 5–10 times atmospheric pressure in the organic layer, 5–15 times atmospheric pressure in the E-layer, 15–20 times atmospheric pressure in the B-layer and 15–30 times atmospheric pressure in the upper C-layer.

For $p_{CO_2}=0.0055$ atm (about 15 times the partial $CO_2$ pressure in air) and $Q=0.3$ m/yr, eq.V.43 yields a bicarbonate leaching of almost 100 eq/ha/yr at pH=5.5, not always a negligible quantity. Therefore, it would make sense to include the bicarbonate leaching into the SMB model. Not only would this make critical loads more compatible with steady-state solutions of dynamic models, but it is also the only way to allow the ANC leaching to obtain positive values! Eq.V.27 would then read:

\[
ANC_{le} = -H_{le} - Al_{le} + HCO_3^{-} = Q \cdot ([HCO_3^{-}] - [H] - [Al])
\]
All chemical criteria could be used, since bicarbonate leaching could always be calculated from $H_e$ via eq.V.43. We illustrate the influence of bicarbonates on the ANC leaching by re-drawing Figure V.4, but now using eq.V.45 to calculate the ANC leaching.

Comparing Figure V.6 with Figure V.4 illustrates that, depending on the parameters of the site, bicarbonate leaching can make a significant contribution to the overall ANC leaching.

**Figure V.6**: Critical ANC leaching (for $Q=1\text{ m/yr}$) including bicarbonate leaching as a function of the critical base saturation, $E_{BC,crit}$, using the same parameters as in Figure V.4.

(c) Including the dissociation of organic acids

The charge balance (eq.V.9) and the definition of ANC leaching in eq.V.10 also include the leaching of organic anions ($RCOO^{-}_{le}$). This has been neglected in the SMB model for (at least) two reasons: (i) to keep the SMB model simple, and/or (ii) assuming that the negatively charged organic anion concentration balances the positively charged organic Al-complexes. However, this does not hold for a wide range of pH values, and at sites with high concentrations of organic matter the contribution of organic anions to ANC leaching can be considerable.

Since it is difficult to characterise (let alone model) the heterogeneous mixture of naturally occurring organic solutes, so-called 'analogue models' are used. The simplest assumes that only monovalent organic anions are produced by the dissociation of dissolved organic carbon:

\[
[RCOO^-] = \frac{m \cdot DO\cdot K_1}{K_1 + [H]} \tag{V.46}
\]

where $DOC$ is the concentration of dissolved organic carbon (in molC/m³), $m$ is the concentration of functional groups (the 'charge density', in mol/molC) and $K_1$ the dissociation constant. Both $DOC$ and $m$ are site-specific quantities. While $DOC$ estimates are often available, data for $m$ are less easy to obtain. For example, Santore et al. (1995) report values of $m$ between 0.014 for topsoil samples and 0.044 mol/molC for a B-horizon in the Hubbard Brook experimental forest in New Hampshire.

Since a single value of $K_1$ does not always model the dissociation of organic acids satisfactorily, Oliver et al. (1983) have derived an empirical relationship between $K_1$ and pH:
\[ pK_1 = -\log_{10} K_1 = a + b \cdot pH - c \cdot (pH)^2 \]

with \( a=0.96 \), \( b=0.90 \) and \( c=0.039 \) (and \( m=0.120 \text{ mol/molC} \)). Note that eq.5.47 gives \( K_1 \) in mol/L. In Figure 5.5 the fraction of \( m\text{DOC} \) dissociated as a function of \( pH \) is shown for the Oliver model and a mono-protic acid with a ‘widely-used’ value of \( pK_1=4.5 \).

Figure V.7 shows that, depending on the amount of DOC, the contribution of organic anions to the ANC leaching, even at fairly low pH, can be considerable.

Other models for the dissociation of organic acids have been suggested and are in use in dynamic models, such as di- and tri-protic analogue models (see, e.g., Driscoll et al. 1994), or more detailed models of the speciation of humic substances, such as the WHAM model (Tipping 1994). Any model could be used for the calculation of critical loads as long as the dissociation depends only on \([H]\), so that a critical leaching of organic anions can be derived from \([H]_{\text{crit}}\) (or \([Al]_{\text{crit}}\)).

### V.4 CRITICAL LOADS FOR AQUATIC ECOSYSTEMS

The purpose of critical loads for aquatic ecosystems is to estimate the maximum deposition(s) below which ‘significant harmful effects’ on biological species do not occur. Similar to terrestrial ecosystems, the links between water chemistry and biological impacts cannot be modelled adequately at present (see also Wright and Lie 2002) as such, water quality criteria are generally used to derive critical loads for aquatic ecosystems.

In this Section we deal only with the modelling of critical loads of acidity for aquatic ecosystems. The models are restricted to freshwater systems, since models for marine ecosystems do not seem to exist. Empirical critical loads of nitrogen for eutrophication for fresh waters, as well as coastal and marine habitats, can be found in Section V.2.

The following description is largely based on the review by Henriksen and Posch (2001), but amended with new or additional information where available. Three models for calculating critical loads of acidifying N and S deposition are described. Models of critical loads for surface waters also include their terrestrial catchments to a greater or lesser extent. Therefore, it is advised to consult Section V.3 for some of the terminology and variables used in the context of critical loads for soils.
V.4.1 THE STEADY-STATE WATER CHEMISTRY (SSWC) MODEL

V.4.1.1 MODEL DERIVATION

The critical load of a lake or stream can be derived from present day water chemistry using the SSWC model, if weighted annual mean values, or estimates thereof, are available. It assumes that all sulphate \(\text{SO}_4^{2-}\) in runoff originates from sea salt spray and anthropogenic deposition (no adsorption or retention). The model uses Acid Neutralising Capacity (ANC) as the variable linking water chemistry to sensitive indicator organisms in freshwaters.

In the SSWC model (Sverdrup et al. 1990, Henriksen et al. 1992, Henriksen and Posch 2001) a critical load of acidity, \(\text{CL}(A)\), is calculated from the principle that the acid load should not exceed the non-marine, non-anthropogenic base cation input and sources and sinks in the catchment minus a buffer to protect selected biota from being damaged, i.e.:

\[
\text{CL}(A) = \text{BC}^*_{\text{dep}} + \text{BC}_w - \text{BC}_u - \text{ANC}_{\text{limit}}
\]

where \(\text{BC}^*_{\text{dep}}(\text{BC}=\text{Ca}+\text{Mg}+\text{K}+\text{Na})\) is the sea-salt corrected (with Cl as a tracer; see Chapter 2) non-anthropogenic deposition of base cations, \(\text{BC}_w\) is the average weathering flux, \(\text{BC}_u(\text{BC}=\text{Ca}+\text{Mg}+\text{K})\) is the net long-term average uptake of base cations in the biomass (i.e., the annual average removal of base cations due to harvesting), and \(\text{ANC}_{\text{limit}}\) the lowest ANC-flux that does not damage the selected biota. Since the average flux of base cations weathered in a catchment and reaching the lake is difficult to measure or to compute from available information, a critical load equation that uses water quality data alone has been derived.

In pre-acidification times the non-marine flux of base cations from the lake, \(\text{BC}_{0}^*\), is given by (all parameters are expressed as annual fluxes, e.g. in eq/m²/yr):

\[
\text{BC}_{0}^* = \text{BC}^*_{\text{dep}} + \text{BC}_w - \text{BC}_u
\]

Thus we have for the critical load from eq.5.48:

\[
\text{CL}(A) = \text{BC}_{0}^* - \text{ANC}_{\text{limit}} = Q \cdot \left(\text{[BC]}^*_0 - \text{[ANC]}_{\text{limit}}\right) ds
\]

where the second identity expresses the critical load in terms of the catchment runoff \(Q\) (in m³/yr) and concentrations \([X]=X/Q\). To estimate the pre-acidification flux of base cations we start with the present flux of base cations, \(\text{BC}^*_t\), given by:

\[
\text{BC}^*_t = \text{BC}^*_{\text{dep}} + \text{BC}_w - \text{BC}_u + \text{BC}_{\text{exc}}
\]

where \(\text{BC}_{\text{exc}}\) is the release of base cations due to ion-exchange processes. Assuming that deposition, weathering rate and net uptake have not changed over time, we obtain \(\text{BC}_{\text{exc}}\) by subtracting eq.V.49 from eq.V.51:

\[
\text{BC}_{\text{exc}} = \text{BC}^*_0 - \text{BC}^*_t
\]

This present-day excess production of base cations in the catchment is related to the long-term changes in inputs of non-marine acid anions by the so-called F-factor (see below):

\[
\text{BC}_{\text{exc}} = F \cdot \left(\Delta \text{SO}_4^* + \Delta \text{NO}_3\right) ds
\]

For the pre-acidification base cation flux we thus get from eq.5.52 \((\Delta X = X_t - X_0)\):

\[
\text{BC}^*_0 = \text{BC}^*_t - F \cdot \left(\Delta \text{SO}_4 - \Delta \text{SO}_4^0 + \Delta \text{NO}_3 - \Delta \text{NO}_3^0\right) da
\]

The pre-acidification nitrate concentration, \(\text{NO}_3\), is generally assumed zero.
V.4.1.2 THE F-FACTOR

According to eqs. V.52 and V.53, and using concentrations instead of fluxes, the F-factor is defined as the ratio of change in non-marine base cation concentrations due to changes in strong acid anion concentrations (Henriksen 1984, Brakke et al. 1990):

\[
F = \frac{([BC^+]_t - [BC^+]_0)}{([SO_4^{2-}]_t - [SO_4^{2-}]_0 + [NO_3^-]_t - [NO_3^-]_0)}
\]

where the subscripts \(t\) and 0 refer to present and pre-acidification concentrations, respectively. If \(F=1\), all incoming protons are neutralised in the catchment (only soil acidification), at \(F=0\) none of the incoming protons are neutralised in the catchment (only water acidification). The F-factor was estimated empirically to be in the range 0.2–0.4, based on the analysis of historical data from Norway, Sweden, U.S.A. and Canada (Henriksen 1984). Brakke et al. (1990) later suggested that the F-factor should be a function of the base cation concentration:

\[
F = \sin\left(\frac{\pi}{2}[BC^+]/[S]\right)
\]

where \([S]\) is the base cation concentration at which \(F=1\); and for \([BC^+]>[S]\) \(F\) is set to 1. For Norway \([S]\) has been set to 400 meq/m\(^3\) (ca. 8 mg Ca/L) (Brakke et al. 1990).

In eq. V.56 the present base cation concentration is used for practical reasons. To render the F-factor independent from the present base cation concentration (and to simplify the functional form), Posch et al. (1993) suggested the following relationship between \(F\) and the pre-acidification base cation concentration \([BC^+]_0\):

\[
F = 1 - \exp\left(-[BC^+]_0/[B]\right)
\]

where \([B]\) is a scaling concentration estimated to be 131 meq/m\(^3\) from paleolimnological data from Finland (Posch et al. 1993). Inserting this expression into eq. 5.55 gives a non-linear equation for \([BC^+_0]\) which has to be solved by an iterative procedure. The two expressions for the F-factor give similar results when used to calculate critical loads for surface waters in Norway (see Henriksen and Posch 2001).

The use of the F-factor, defined as a function of the base cation concentration (Henriksen 1984) was originally derived from Norwegian lake data. In Norway the range of runoff is wide (0.3–5 m/yr), with an average of about 1 m/yr. In other Nordic countries, such as Sweden and Finland, runoff is low compared to most of Norway. The weathering rate of a catchment is largely dependent on the bedrock and overburden. Thus, catchments with similar bedrock and overburden characteristics should have similar weathering rates. If one catchment has a high runoff, e.g., 2 m/yr, and another one has a low runoff, e.g., 0.3 m/yr, their base cation fluxes will be similar, but their concentrations will differ considerably. Thus, in the F-factor (eq.5.56) the BC-flux should be used instead of the concentration (Henriksen and Posch 2001):

\[
F = \sin\left(\frac{\pi}{2}Q\cdot[BC^+_0]/[S]\right)
\]

where \(S\) is the base cation flux at which \(F=1\). For Norway, \(S\) has been estimated at 400 meq/m\(^2\)/yr. Again, if \(Q\cdot[BC^+_0]>S\), \(F\) is set to 1. Similarly, fluxes could be introduced for the formulation in eq. V.57.

V.4.1.3 THE NON-ANTHROPOGENIC SULPHATE CONCENTRATION

The pre-acidification sulphate concentration in lakes, \([SO_4^{2-}]_0\), is assumed to consist of a constant atmospheric contribution and a geologic contribution proportional to the concentration of base cations (Brakke et al. 1989):

\[
[SO_4^{2-}]_0 = a + b\cdot[BC^+]
\]

The coefficients in this equation, estimated for different areas and by different authors, are summarised in Table V.14.
Table V.14: Constants to estimate the non-anthropogenic sulphate concentration with eq. V.59, derived from empirical data (N is the number of samples and r is the correlation coefficient).

<table>
<thead>
<tr>
<th>a (meq/m³)</th>
<th>b</th>
<th>N</th>
<th>r</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.16</td>
<td>143</td>
<td>0.38</td>
<td>Lakes, Norway (Brakke et al. 1989)</td>
</tr>
<tr>
<td>8</td>
<td>0.17</td>
<td>289</td>
<td>0.78</td>
<td>Lakes, Norway (Henriksen and Posch 2001)</td>
</tr>
<tr>
<td>5</td>
<td>0.05</td>
<td>n.g.</td>
<td>n.g.</td>
<td>Groundwater, Sweden (Wilander 1994)</td>
</tr>
<tr>
<td>14</td>
<td>0.10</td>
<td>61</td>
<td>0.29</td>
<td>Lakes, Finland (Posch et al. 1993)</td>
</tr>
<tr>
<td>19</td>
<td>0.08</td>
<td>251</td>
<td>0.66</td>
<td>Lakes, N. Norway+Finland+Sweden (Posch et al. 1997)</td>
</tr>
<tr>
<td>9.5</td>
<td>0.08</td>
<td>60</td>
<td>0.66</td>
<td>Lakes, Ireland (Aherne et al. 2002)</td>
</tr>
</tbody>
</table>

Details on the procedures and data sources for estimating these coefficients can be found in the references given. In Henriksen and Posch (2001) it is shown that the exceeded area for Norwegian lakes (in 1994) is influenced very little by the choice of coefficients for calculating non-anthropogenic sulphate. Similar results have been reported for Irish lakes (Aherne and Curtis 2003).

Larssen and Høgåsen (2003) suggested that the atmospheric contribution in eq. V.59 be derived from background S deposition, as estimated by atmospheric transport models:

\[
(SO_4^2^-)_0 = \frac{S_{dep,0}}{Q + b \cdot BC},
\]

For southern Norway, \( S_{dep,0} \) is about 50 mgS/m²/yr from the EMEP long-range transport model, i.e., about 3 meq/m²/yr. With \( Q \) varying between 0.5 and 1 m/yr this results in an atmospheric contribution to \([SO_4^2^-]_0\) of about 3–6 meq/m³.

V.4.1.4 THE ANC-LIMIT

Lien et al. (1996) analysed the status of fish and invertebrate populations in the context of surface water acidification and loss of ANC in Norwegian lakes and streams. The data for fish came from populations in 1095 lakes, mostly from the regional lake survey carried out in 1986 (Henriksen et al. 1988, 1989). The critical level of ANC varied among fish species, with Atlantic salmon being the most sensitive, followed by brown trout. They concluded that Atlantic salmon appeared to be a good indicator of acidification of rivers, and trout seemed to be a useful indicator for acidification of lakes. Based on an evaluation of fish and invertebrate populations, a critical lower limit of \([ANC]=20\) meq/m³ was suggested as the tolerance level for Norwegian surface waters (Lien et al. 1996; see Figure V.8). This limit has been widely used (Kola, northern Russia: Moiseenko 1994; southern central Alps: Boggero et al. 1998; China: Duan et al. 2000); however, it has been set to zero in the United Kingdom (CLAG 1995) and to 40 meq/m³ in south-central Ontario, Canada (Henriksen et al. 2002).

The SSWC model has been developed for and is particularly applicable to dilute oligotrophic waters located on granitic and gneissic bedrock with thin overburden, such as large parts of Fennoscandia, Scotland, Canada and Ireland. In such areas, surface waters are generally more sensitive to acid inputs than soils. The model assumes that all sulphate in runoff originates from deposition alone, except for a small geologic contribution. In areas where the geological conditions lead to more alkaline waters, the SSWC model has to be modified, since significant amounts of sulphate from geological sources can be present in the runoff water. A modification for this kind of conditions has been developed for Slovakia (Závodský et al. 1995).
Lydersen et al. (2004) argued that the ANC-limit should be corrected with the amount of organic acids present in the lake. They showed that the fit between observed fish status and ANC can be (slightly) improved, if an ‘organic acid adjusted’ ANC, $[\text{ANC}]_{\text{oaa}}$, is used (instead of the ‘standard’ ANC). They define this quantity as:

$$[\text{ANC}]_{\text{oaa}} = [\text{ANC}] - \frac{1}{5} \cdot m \cdot \text{TOC}$$

where $m \cdot \text{TOC}$ is the total organic carbon expressed in meq/m$^3$ ($m$ being the charge density). Such a correction leads to a lower ANC-limit, i.e., higher critical loads.

Figure V.8 indicates that in the ANC range 0–50 meq/m$^3$ there is a decreasing probability from about 50 to 0% of damage to fish populations. The lakes studied receive very low to very high (for Norway) levels of deposition, thus including a wide range of affected lakes. This implies that for a given ANC-value lakes of varying sensitivity exist, receiving varying amounts of deposition. This could reflect that fish have responded to the same ANC differently in different lakes, indicating that a catchment-dependent ANC-limit would be more appropriate than a fixed value for all lakes. In other words, every lake has its own characteristic ANC-limit (in the range shown in Figure V.8). Less sensitive lakes, i.e., lakes with higher critical loads, should have a higher ANC-limit, since less sensitive ecosystems will have a higher biological variety/diversity and thus require a higher ANC-limit to keep that diversity intact. The simplest functional relationship with this feature is a linear relationship between $[\text{ANC}]_{\text{lim}}$ and the critical load $CL$:

$$[\text{ANC}]_{\text{lim}} = k \cdot CL$$

This gives the following implicit equation for the critical load (see eq.5.50):

$$CL = Q \cdot (BC^*) - k \cdot CL$$

which yields after re-arranging for $CL$:

$$CL = Q \cdot (BC^*)_0 / (1 + k \cdot Q)$$

and thus from eq.5.62:

$$[\text{ANC}]_{\text{lim}} = k \cdot Q \cdot (BC^*)_0 / (1 + k \cdot Q)$$

This is a special case of a more general expression derived earlier using somewhat different arguments (Henriksen et al. 1995). As for the constant $[\text{ANC}]_{\text{lim}}$, used earlier, the proportionality constant $k$ should be derived from data. If we assume that for $CL=0$, the $[\text{ANC}]_{\text{lim}}=0$; if we further assume that for a critical load of 200 meq/m$^2$/yr the ANC-limit should not exceed 50 meq/m$^3$, as has been assumed in Sweden, we arrive at a $k$-value of 50/200 = 0.25 yr/m. In addition, for $CL$-values above 200 meq/m$^2$/yr we set the $[\text{ANC}]_{\text{lim}}$ to the constant value of 50 meq/m$^3$. The value of $k$ is derived from experience in the Nordic countries and, as such, reflects the geology, deposition history and biological diversity (fish species) of that region. For different regions other $k$-values may be more appropriate.
V.4.2 THE EMPIRICAL DIATOM MODEL

The empirical diatom model is an alternative approach to the SSWC model and is developed from paleolimnological data (Battarbee et al. 1995). Diatom assemblages in cores from acidified lakes usually show that prior to acidification the diatom flora, and therefore water chemistry, changed little over time. The point of acidification is indicated by a shift towards a more acidophilous diatom flora. Diatoms are amongst the most sensitive indicators of acidification in freshwater ecosystems, hence it can be argued that the point of change in the diatom record indicates the time at which the critical load for the site was exceeded.

The acidification status (as defined by diatom analyses) of 41 sites in the United Kingdom (UK) was compared to site sensitivity (defined by lake-water calcium concentrations) and current deposition loading. The optimal separation of acidified and non-acidified sites is given by a [Ca]:S<sub>dep</sub> ratio of 94:1 (Battarbee et al. 1995), acidified sites having a ratio less than 94:1. This critical ratio, determined by logistic regression, can be used to define critical sulphur loads for any site, including streams. Critical load values are calculated from pre-acidification calcium concentrations using the F-factor (Brakke et al. 1990). For example, the critical sulphur load for a lake with a [Ca]<sub>0</sub>-value of 40 meq/m<sup>3</sup> is approximately 0.43 keq/ha/yr.

The diatom model has been adapted to provide critical loads, and critical load exceedances, for total acidity (sulphur and nitrogen). Exceedance values for total acidity require a measure of the fraction of deposited nitrogen leached to the surface waters. This is calculated from the differences between the ratios of sulphate/nitrate in the water and in the deposition at the site. In this way the fraction of the nitrogen deposition contributing to acidification, a<sub>N</sub>, is added to the value of sulphur deposition to provide a total ‘effective’ acid deposition:

(V.66) \[ a_N = \frac{S_{dep}^*}{N_{dep}} \left[ \frac{SO_4^1}{NO_3^-} \right] \]

This model assumes equilibrium between sulphur deposition and sulphate in water, and only applies to sites with no additional catchment nitrogen inputs. The diatom model has been re-calibrated for total acidity loads by substituting total effective acid deposition for sulphur deposition. The resulting critical ratio is 89:1, slightly lower than when considering sulphur alone. The basic equation for the critical load of total acidity in the empirical diatom model is therefore as follows:

(V.67) \[ CL(A) = \frac{[Ca^+]_{0}}{89} \]

where \( CL(A) \) is in keq/ha/yr and \([Ca^+]_{0}\) in meq/m<sup>3</sup>. The pre-acidification Ca-concentration is calculated as:

(V.68) \[ [Ca^+]_{0} = [Ca^+] - F_{Ca} [SO_4^1] - [NO_3^-] + [NO_3^-]_{0} \]

with

(V.69) \[ F_{Ca} = \sin \left(\frac{[Ca^+]_{0}}{[S_{Ca}]} \right) \]

and \([S_{Ca}]\) is the Ca-concentration at which \( F_{Ca} = 1 \). It can vary between 200 and 400 meq/m<sup>3</sup>, depending on location. In the UK critical loads mapping exercise a value of \([S_{Ca}] = 400\) meq/m<sup>3</sup> has been used, and in waters with \([Ca^+] > [S_{Ca}], F_{Ca} \) was set to 1. The pre-acidification nitrate concentration, \([NO_3^-]_{0}\), is assumed zero. The pre-acidification sea-salt corrected sulphate concentration, \([SO_4^1]_{0}\), is estimated according to eq.V.59 (Brakke et al. 1989).

The diatom model has been calibrated using sites and data from the UK. However, a major advantage of the approach is that predictions for any lake can be validated by analysing diatoms in a sediment core. In this way the applicability of the model to sites outside the UK can be tested.
V.4.3 THE FIRST-ORDER ACIDITY BALANCE (FAB) MODEL

The First-order Acidity Balance (FAB) model for calculating critical loads of sulphur (S) and nitrogen (N) for a lake takes into account sources and sinks within the lake and its terrestrial catchment. The original version of the FAB model has been developed and applied to Finland, Norway and Sweden in Henrikson et al. (1993) and further described in Posch et al. (1997). A modified version was first reported in Hindar et al. (2000) and is described in Henrikson and Posch (2001). The FAB model is designed to be equivalent to the Simple Mass Balance model for a catchment, and it largely follows its derivation (see Section V.4), the main difference being that the leaching of ANC is modelled according to the SSWC model (see section V.5.1).

V.4.3.1 MODEL DERIVATION

The lake and its catchment are assumed small enough to be properly characterised by average soil and lake water properties. With \( A \) we denote the total catchment area (lake + terrestrial catchment), \( A_l \) is the lake area, \( A_f \) the forested area and \( A_g \) the area covered with grass/heath land. We have \( A_l + A_f + A_g \leq A \), and a non-zero difference represents a land area on which no transformations of the deposited ions take place ('bare rock').

Starting point for the derivation of the FAB model is the charge balance ('acidity balance') in the lake water running off the catchment:

\[
S_{\text{runoff}} + N_{\text{runoff}} = BC^{\text{runoff}} - A_{\text{ANC}}^{\text{runoff}}
\]

where \( BC^\ast \) stands for the sum of (non-marine) base cations and ANC is the acid neutralising capacity. In the above equation we assume that the quantities are total amounts per time (e.g. eq/yr). In order to derive critical loads we have to link the ions in the lake water to their depositions, taking into account their sources and sinks in the terrestrial catchment and in the lake.

For \( X = S, N \) and \( BC \) the mass balance in the lake is given by:

\[
X_{\text{runoff}} = X_{\text{in}} - X_{\text{ret}}, \quad X = S, N, BC
\]

where \( X_{\text{in}} \) is the total amount of ion \( X \) entering the lake and \( X_{\text{ret}} \) the amount of \( X \) retained in the lake. The in-lake retention of \( S \) and \( N \) is assumed to be proportional to the input of the respective ion into the lake:

\[
X_{\text{ret}} = \rho_X \cdot X_{\text{in}}, \quad X = S, N
\]

where \( 0 \leq \rho_X \leq 1 \) is a dimensionless retention factor. Thus the mass balances for the lake become:

\[
X_{\text{runoff}} = (1 - \rho_X) \cdot X_{\text{in}}, \quad X = S, N
\]

The total amount of sulphur entering the lake is given by:

\[
S_{\text{in}} = A \cdot S_{\text{dep}}
\]

where \( S_{\text{dep}} \) is the total deposition of S per unit area. Immobilisation, reduction and uptake of sulphate in the terrestrial catchment are assumed negligible, and sulphate ad/desorption is not considered since we model steady-state processes only.

Eq.V.74 states that all sulphur deposited onto the catchment enters the lake, and no sources or sinks are considered in the terrestrial catchment.

In the case of nitrogen we assume that immobilisation and denitrification occur both in forest and grass/heath land soils, whereas net uptake occurs in forests only (equalling the annual average amount of N lost by harvesting); the deposition onto the remaining area (lake + 'bare rocks') enters the lake unchanged. Thus the amount of N entering the lake is:

\[
N_{\text{in}} = (A - A_f - A_g) \cdot N_{\text{dep}}
\]

\[
+ A_f \cdot (N_{\text{dep}} - N_i - N_u - N_{\text{de}}),
\]

\[
+ A_g \cdot (N_{\text{dep}} - N_i - N_{\text{de}}),
\]

where \( N_{\text{dep}} \) is the total N deposition, \( N_i \) is the long-term net immobilisation of N (which may include other long-term steady-state sources and sinks; see Chapter 5.3), \( N_{\text{de}} \) is N lost by denitrification, and \( N_u \) the net growth uptake of N, all per unit area. The symbol \( (x)_i \) or \( x_i \),
is a short-hand notation for max(x, 0), i.e., x_+= x for x > 0 and x_− = 0 for x ≤ 0. The effects of nutrient cycling are ignored and the leaching of ammonium is considered negligible, implying its complete uptake and/or nitrification in the terrestrial catchment.

While immobilisation and net growth uptake are assumed independent of the N deposition, denitrification is modelled as fraction of the available N:

\[(5.76)\]

\[N_{de} = \begin{cases} f_{de} \cdot (N_{dep} - N_i - N_u) & \text{on } A_f \\ f_{de} \cdot (N_{dep} - N_i) & \text{on } A_g \end{cases}\]

where 0 ≤ f_{de} < 1 is the (soil-dependent) denitrification fraction. The above equation is based on the assumption that denitrification is a slower process than immobilisation and growth uptake. Inserting eq.5.76 into eq.5.75 one obtains:

\[(5.77)\]

\[N_{in} = (A - A_f - A_g) \cdot N_{dep} + A_f \cdot (1 - f_{de}) \cdot (N_{dep} - N_i) + A_g \cdot (1 - f_{de}) \cdot (N_{dep} - N_i),\]

If sufficient data for quantifying the sources and sinks of base cations in the catchment, such as deposition, weathering and uptake, are available, the runoff of base cations (BC_{runoff}) could be described in the same way as S and N. This would be in analogy to the derivation of the SMB model for (forest) soils. Alternatively, water quality data can be used to quantify the runoff of base cations and ANC, as is done in the SSWC model (see section 5.5.1).

To arrive at an equation for critical loads, a link has to be established between a chemical variable and effects on aquatic biota. The most commonly used criterion is the so-called ANC-limit (see above), i.e. a minimum concentration of ANC derived to avoid ‘harmful effects’ on fish: ANC_{runoff,crit} = A \cdot Q \cdot [ANC]_{limit}.

Defining \( L_{crit} = (BC_{runoff} - ANC_{runoff,crit})/A \), inserting eq.5.74 and 5.77 into eq.5.73 and eq.5.70 and dividing by A yields the following equation to be fulfilled by critical depositions (loads) of S and N:

\[(5.78)\]

\[1 - \rho_s \cdot S_{dep} + (1 - \rho_N) \cdot (1 - f - g) \cdot N_{dep} + f \cdot (1 - f_{de}) \cdot (N_{dep} - N_i - N_u) + g \cdot (1 - f_{de}) \cdot (N_{dep} - N_i) = L_{crit}\]

where we have defined:

\[(5.79)\]

\[f = A_f / A, \quad g = A_g / A\]

\[\Rightarrow \quad 1 - f - g \geq r \quad \text{with} \quad r = A_i / A\]

Eq.5.78 defines a function in the (N_{dep}, S_{dep})-plane, the so-called critical load function (see Figure 5.7), and in the following we will look at this function in more detail. The general form of the critical load function is:

\[(5.80)\]

\[a_s \cdot S_{dep} + a_N \cdot N_{dep} = L_N + L_{crit}\]

with

\[(5.81)\]

\[a_s = 1 - \rho_s, \quad a_N = (1 - \rho_N) \cdot b_N, \quad L_N = (1 - \rho_N) \cdot M_N\]

The quantity \( M_N \) and the dimensionless coefficient \( b_N \) depend on \( N_{dep} \):

(a) \( N_{dep} \leq N_i \): In this case (\( N_{dep} - N_i \))_+ = 0 and (\( N_{dep} - N_i - N_u \))_+ = 0, which means that all N falling onto forests and grassland is immobilised and only the N deposition falling directly onto the lake and ‘bare rocks’ contributes to the leaching of N:

\[(5.82)\]

\[b_N = b_1 = 1 - f - g, \quad M_N = M_1 = 0\]

(b) \( N_i < N_{dep} \leq N_i + N_u \): In this case (\( N_{dep} - N_i \))_+ = N_{dep} - N_i, but (\( N_{dep} - N_i - N_u \))_+ = 0, meaning that all N deposition falling onto forests is immobilised or taken up, but N falling onto the other areas is (partially) leached:

\[(5.83)\]

\[b_N = b_2 = 1 - f - g \cdot f_{de}, \quad M_N = M_2 = (1 - f_{de}) \cdot g \cdot N_i\]

(c) \( N_{dep} > N_i + N_u \): Some N deposition is leached from all areas:
The maximum critical load of sulphur is obtained by setting $N_{\text{dep}} = 0$ in eq. 5.78:

$$ CL_{\text{max}}(S) = L_{\text{crit}} / a_S $$

Setting $S_{\text{dep}} = 0$ and considering the three different cases for $N_{\text{dep}}$, gives the following expression for the maximum critical load for nitrogen:

$$ CL_{\text{max}}(N) = \min\left\{\left(\frac{L_{\text{crit}}}{(1 - \rho_i) + M_i}\right) / b_i, i = 1, 2, 3\right\} $$

Figure V.9: Piece-wise linear critical load function of S and acidifying N for a lake as defined by catchment properties. Note the difference with the critical load function for soils (see Figure 5.3). The grey area below the CL function denotes deposition pairs resulting in an ANC leaching greater than $Q \cdot [\text{ANC}]_{\text{lim}}$ (non-exceedance of critical loads; see Chapter VII).

### V.4.3.2 SYSTEMS OF LAKES

The above derivation of the FAB model is for (small) headwater lakes only. Critical loads are generally calculated for such lakes, since lakes with (many) upstream lakes tend to have larger catchments, and several (implicit) assumptions of the FAB model, e.g. uniform depositions, will be violated. Nevertheless, in some areas systems of lakes can be found on a small scale, and therefore a model for such systems is desirable.

When computing the critical load of acidity with the SSWC model (which uses annual average lake water chemistry) for a lake receiving runoff from upstream lakes, one implicitly computes the critical load for that lake including all its upstream lakes, since water samples taken from (the outlet of) the lowest lake is a mixture of the water of that lake and all its upstream lakes. Consequently, when applying the FAB model to such a lake, one has to be aware that one also computes the critical load for the whole system of lakes and thus must take into account the catchment and lake characteristics of all lakes in the system. To do this in a more explicit way, two methods for computing the critical load of a system of lakes have been developed (Hindar et al. 2000). Both require the same input data, but they differ in the complexity of the calculations involved. The formulae will not be derived here, and the interested reader is referred to the literature (see also Hindar et al. 2001), where also the differences between the methods are demonstrated, using data from lake systems in the Killarney Provincial Park in Ontario, Canada. An application to lakes in the Muskoka river catchment (Ontario, Canada) can be found in Aherne et al. (2003).
V.4.4 INPUT DATA

In addition to the data required for the SSWC and diatom model (runoff and concentrations of major ions in the lake runoff water), the FAB model needs also information on (a) the area of lake, catchment and different land cover classes, (b) terrestrial nitrogen sinks, and (c) parameters for in-lake retention of N and S.

V.4.4.1 RUNOFF

The runoff $Q$ is the amount of water leaving the catchment at the lake outlet, expressed in m/yr. It is derived from measurements or can be calculated as the difference between precipitation and actual evapotranspiration, averaged over the catchment area. A long-term climatic mean annual value should be taken. Sources for data and models for evapotranspiration can be found in Section V.5.

V.4.4.2 ION CONCENTRATIONS

In addition to runoff, the concentrations of major ions in the runoff water, i.e. sulphate, nitrate and base cations, are needed to calculate SSWC critical loads, and these come from the analysis of representative water samples.

The critical load for a site should be calculated with yearly flow-weighted average chemistry and yearly average runoff. Since such values are not available for a large number of lakes, critical loads are mostly calculated on the basis of a single sample considered representative of yearly flow-weighted averages. A sample collected shortly after the fall circulation of a lake is generally assumed to fulfil this purpose. To check this claim, Henriksen and Posch (2001) compared critical load values calculated from yearly flow-weighted average concentrations with critical loads calculated from a single fall value for sites for which long-term data series are available. Results for seven Norwegian catchments show that the single fall value is fairly representative for the annual average chemistry. Similarly, results from eight Canadian catchments show that a single spring sample is fairly representative of the annual average chemistry (Henriksen and Dillon 2001).

V.4.4.3 LAKE AND CATCHMENT CHARACTERISTICS

The area parameters $A$, $A_l$, $A_f$ and $A_g$, which are needed in the FAB model, can generally be derived from (digital or paper) maps.

V.4.4.4 TERRESTRIAL NITROGEN SINKS

The uptake of N can be computed from the annual average amount of N in the harvested biomass. If there is no removal of trees from the catchment, $N_i = 0$.

$N_i$ is the long-term annual immobilisation (accumulation) rate of N in the catchment soil. Note that at present immobilisation may be substantially higher due to elevated N deposition.

V.4.4.5 IN-LAKE RETENTION OF N AND S

Concerning in-lake processes, the retention factor for nitrogen $\rho_N$ (see eq.V.72) is modelled by a kinetic equation (Kelly et al. 1987):

$$\rho_N = \frac{s_N}{s_N + z/\tau} = \frac{s_N}{s_N + Q/r}$$

where $z$ is the mean lake depth, $\tau$ is the lake’s residence time, $r$ is the lake:catchment ratio ($=A_l/A$) and $s_N$ is the net mass transfer coefficient. There is a lack of observational data for the mass transfer coefficients, especially from European catchments, but Dillon and Molot (1990) give a range of 2–8
m/yr for $s_N$. Values for Canadian and Norwegian catchments are given in Kaste and Dillon (2003).

An equation analogous eq.V.87 for $\rho_S$ with a mass transfer coefficient $s_S$ is used to model the in-lake retention of sulphur. Baker and Brezonik (1988) give a range of 0.2–0.8 m/yr for $s_S$.

V.5 CRITICAL LOADS OF CADMIUM, LEAD AND MERCURY

V.5.1 GENERAL METHODOLOGICAL ASPECTS OF MAPPING CRITICAL LOADS OF HEAVY METALS

V.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 V.15, which is however not a complete review of possible effects of these metals. Indicators of effects on ecosystems listed in Table V.15 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 V.5.2.2.1, protects at the same time against effects on human health via other food and fodder crops (including also the quality of animal products, since the pathway of Cd to wheat leads to the lowest critical Cd content in soils according to De Vries et al. (2003). Such critical load calculations are in principle also possible for lead, and for other food and fodder crops, if the soil-plant transfer can be described with sufficient accuracy and can be done in addition on a voluntary basis.

Among terrestrial ecosystems, critical loads of Cd and Pb are to be calculated from the viewpoint of ecotoxicology for areas covered by non-agricultural land (forests, seminatural 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 V.5.2.1.
For aquatic ecosystems the critical limits of \( \text{Pb} \) and \( \text{Cd} \) are related to ecotoxicological effects, while human health effects by this pathway are less relevant and therefore not considered here. Critical limits of \( \text{Hg} \) refer to both human health effects (\( \text{Hg} \) concentration in fish and other animals that serve as a food source to humans) and ecotoxicological effects, since microbiota and higher wildlife itself may also be affected.

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

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

If different indicators within each category (map) have been considered (e.g. \( \text{Cd} \) in wheat and \( \text{Cd} \) in soil drainage water in view of ground water protection for human health), the final map should indicate the minimum critical \( \text{Cd} \) 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

---

**Table V.15: Four types of critical loads of Pb, Cd, Hg, related receptors and indicators**

<table>
<thead>
<tr>
<th>Receptor ecosystem</th>
<th>Critical related to</th>
<th>Metals of concern</th>
<th>Land types to be considered</th>
<th>Indicator addressed by the critical limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Terrestrial (*)</td>
<td>a) Human health effects</td>
<td>( \text{Cd, Pb, Hg} )</td>
<td>Arable land, grassland</td>
<td>Metal content in food/fodder crops</td>
</tr>
<tr>
<td></td>
<td>b) Ecosystem functioning</td>
<td>( \text{Pb, Cd, Hg} )</td>
<td>Arable land, grassland, non-agricultural land</td>
<td>Metal content in grass, animal products (cow, sheep)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Total metal concentration in soil water below the rooting zone (aiming at ground water protection</td>
</tr>
<tr>
<td>2) Aquatic</td>
<td>a) Human health effects</td>
<td>( \text{Hg} )</td>
<td>Freshwaters</td>
<td>Metal concentration in fish</td>
</tr>
<tr>
<td></td>
<td>b) Ecosystem functioning</td>
<td>( \text{Pb, Cd, Hg} )</td>
<td>Freshwaters</td>
<td>Total metal concentration in freshwaters in view of effects on algae, crustacea, worms, fish, top predators</td>
</tr>
</tbody>
</table>

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

V.5.1.2 LIMITATIONS IN SITES CALCULATIONS

Critical load calculations cannot 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.

V.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.

V.5.1.3.1 DEFINITIONS

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

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

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

### V.5.1.3.2 SOME GENERAL SYMBOLS AND ABBREVIATIONS:

- \( M \) = a flux of a metal M
- \([M]\) = a content (in soil, plants, other biota) or a concentration (in a liquid) of a metal M
- \([M]_{\text{(crit)}}\) = a critical content (in soil, plants, other biota) or a critical concentration (in a liquid) of a metal M, not explained in the table
- \( f \) = a fraction
- \( c \) = a factor for conversion of units, not explained in the table
- \( \text{sdw} \) = in soil drainage water
- \( \text{sw} \) = in surface water

#### Table V.16: Symbols and abbreviations used in the calculation of critical loads of heavy metals

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>([M]<em>{\text{SPM,sdw}}) or ([M]</em>{\text{SPM,sw}})</td>
<td>Concentration of metal bound to suspended particulate matter in soil drainage water, or in surface water, respectively</td>
<td>mg kg(^{-1})</td>
</tr>
<tr>
<td>([\text{Hg}]_{\text{OM}})</td>
<td>Concentration of Hg, normalised for ([\text{OM}]_{s})</td>
<td>mg (kg OM(^{-1}))</td>
</tr>
<tr>
<td>([\text{Hg}]_{\text{Pike}})</td>
<td>Hg concentration in the flesh of 1-kg pike</td>
<td>mg kg(^{-1}) fw</td>
</tr>
<tr>
<td>([\text{Hg}]_{\text{Bio}})</td>
<td>Hg concentration in biota, e.g. fish flesh</td>
<td>mg kg(^{-1}) fw</td>
</tr>
<tr>
<td>([\text{Hg}]_{\text{Prec}})</td>
<td>Hg concentration in precipitation</td>
<td>ng l(^{-1})</td>
</tr>
<tr>
<td>[clay]</td>
<td>Clay content of the soil</td>
<td>kg clay kg(^{-1}) or %</td>
</tr>
<tr>
<td>([\text{OM}]_{s})</td>
<td>Organic matter content of the soil</td>
<td>kg OM kg(^{-1}) or %</td>
</tr>
<tr>
<td>([\text{DOM}]<em>{\text{sdw}}) or ([\text{DOC}]</em>{\text{sdw}})</td>
<td>Concentration of dissolved organic matter, or dissolved organic carbon, respectively, in soil drainage water</td>
<td>g m(^{-3}) or mg l(^{-1})</td>
</tr>
<tr>
<td>([\text{TOC}]_{\text{sw}})</td>
<td>Concentration of total organic carbon in surface water</td>
<td>g m(^{-3}) or mg l(^{-1})</td>
</tr>
<tr>
<td>([\text{TP}]_{\text{sw}})</td>
<td>Concentration of total phosphorus in surface water</td>
<td>µg l(^{-1}) or mg l(^{-1})</td>
</tr>
<tr>
<td>([\text{SPM}]<em>{\text{sdw}}) or ([\text{SPM}]</em>{\text{sw}})</td>
<td>Concentration of suspended particulate matter in soil drainage water, or in surface water, respectively</td>
<td>kg m(^{-3})</td>
</tr>
<tr>
<td>pH(<em>{\text{sdw}}) or pH(</em>{\text{sw}})</td>
<td>pH value in soil drainage water, or in surface water</td>
<td>-</td>
</tr>
</tbody>
</table>

### V.5.1.4 STAND-STILL APPROACH VERSUS CALCULATION OF CRITICAL LIMIT EXCEEDANCE

The harmonised methodological basis for a first preliminary calculation and mapping of critical loads of Cd and Pb related to ecotoxicological effects (Hettelingh et al. 2002), was based on a guidance document (De Vries et al. 2002). In this document a standstill approach, which aims at avoiding any (further) accumulation of heavy metals in the soil, was also included as an alternative to the effect-based approach. This method is, however, not included in this manual since it implies the continued addition of metals on historically polluted soils with high leaching rates. The current leaching may then already imply significant effects, both on terrestrial as well as aquatic ecosystems receiving the drainage water from the surrounding soils, and is thus not per se acceptable in the long term. Furthermore, it does lead to critical load exceedance at soils
which strongly adsorb heavy metals, whereas the effect does occur through the soil solution. Instead, it is suggested to calculate critical concentrations of metals in the soil, the soil drainage water or the surface water based on the critical limits and compare these to the present soil or water metal concentrations to assess the critical limit exceedance in the present situation. This implies that one has to map the present metal concentrations in the country (expressed as total or reactive soil contents, total dissolved concentrations or even free ion concentrations). Such a comparison can be seen as an intermediate step for dynamic models for heavy metals. If the present soil metal content exceeds the critical concentration (limit), the metal input has to be less than the critical load to reach the critical concentration at a defined time period. In the reverse case, the metal input can be larger than the critical load for a defined time period not exceeding during that period the critical concentration. However, only keeping the critical load will not lead to exceedance of the critical limit in the long run. More information on how to calculate the critical concentration is given in the background document (De Vries et al, 2005).

V.5.2 TERRESTRIAL ECOSYSTEMS

V.5.2.1 SIMPLE STEADY-STATE MASS BALANCE MODEL AND RELATED INPUT DATA

V.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:

\[
\text{CL}(M) = \text{M}_u + \text{M}_{\text{le(crit)}}
\]

where:

\[
\text{CL}(M) = \text{critical load of a heavy metal } M \quad \text{(g ha}^{-1} \text{a}^{-1})
\]

\[
\text{M}_u = \text{metal net uptake in harvestable parts of plants under critical load conditions} \quad \text{(g ha}^{-1} \text{a}^{-1})
\]

\[
\text{M}_{\text{le(crit)}} = \text{critical leaching flux of heavy metal } M \text{ from the considered soil layer} \quad \text{(g ha}^{-1} \text{a}^{-1})
\]

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 \( \text{M}_{\text{le(crit)}} \) refers to the total vertical leaching rate, including dissolved, colloidal and particulate (metal) species in the drainage water. For a critical load, the critical metal leaching is based on a critical (toxic) metal concentration in soil or the (free ion or total) metal concentration in soil water.

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

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

- For Pb and Cd it is assumed that ecotoxicological effects as well as the main proportion of uptake by plants occur in (from) the organic layer (O horizon) and the humus rich (top)soil horizons (A_h, A_p). Therefore the depth of the biological active topsoil (z_b) should be considered for arable land, grass-land, and forests as far as the critical load calculations are addressing ecotoxicological effects, or the protection of food/fodder quality, respectively. For forest soils covered by an organic layer, the critical loads for both the organic layer, and the upper mineral horizon should be calculated separately. In these cases the most sensitive of both layers should be presented in the critical loads map. For all terrestrial ecosystems the maximum depth of the topsoil (z_b) to be considered is the lower boundary of the uppermost mineral horizon (in most soil classification systems called the A-horizon).

Default values of z_b are:

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

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

Note, that for calculations of critical loads with respect to protection of groundwater quality the entire soil column has to be included. However, it is preliminarily not planned within the critical loads work to model the whole pathway of the metal flux with drainage water, considering the binding capacity of layers between rooting zone and upper groundwater. Therefore, for simplification the critical leaching of metals from the viewpoint of ground water protection is calculated by multiplying the drainage water flux below the rooting zone (soil depth = z) with the critical limit for drinking water (see V.5.2.2.2).

V.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 V.5.2.2.1).

Therefore a simplified approach is proposed to describe the tolerable removal of heavy metals by biomass net uptake. The average yield (or growth increment) of harvestable
biomass is multiplied with the heavy metal content in harvestable plant parts and with a factor to account for the fraction of metal uptake from the relevant soil layer relative to the uptake from the total rooting zone (eq. V.89):

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

where:

\( M_u \) = metal net uptake in harvestable parts of plants under critical load conditions (g ha\(^{-1}\) a\(^{-1}\)) (see Eq. V.88).

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

\( Y_{ha} \) = yield of harvestable biomass (dry weight) (kg 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 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 V.17 can be used for orientation, e.g. the average of a range.

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

If contents are available for different harvested parts of the plants (e.g. stem and bark), a mass weighted mean should be used. Beware that only the net uptake is calculated. For instance, for agricultural land the amount of metals in stalks or the leaves of beets remaining on the field should not be considered. The removal of heavy metals in 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.
Table V.17: Ranges of mean values (averages, medians) of contents of Pb, Cd, and Hg in biomass for various species (harvestable parts)

<table>
<thead>
<tr>
<th>Land use</th>
<th>Species</th>
<th>Pb</th>
<th>Cd</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grassland</td>
<td>mixed grassland species</td>
<td>1.0 - 3.0</td>
<td>0.05 - 0.25</td>
<td>0.01 - 0.1</td>
</tr>
<tr>
<td>Arable land</td>
<td>wheat (grains)</td>
<td>0.1</td>
<td>0.08</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>other cereals (grains)</td>
<td>0.1 - 0.3</td>
<td>0.02 - 0.06</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>potato</td>
<td>0.73</td>
<td>0.23</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>sugar beet</td>
<td>1.0</td>
<td>0.25</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>maize</td>
<td>3.8</td>
<td>0.2</td>
<td>0.04</td>
</tr>
<tr>
<td>Coniferous forest</td>
<td>spruce, pine, fir, douglas, Central Europe</td>
<td>0.5 - 10</td>
<td>0.1 - 0.5</td>
<td>0.01 - 0.05*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1/0.2**</td>
<td>0.02/0.04**</td>
<td>0.004/0.008**</td>
</tr>
<tr>
<td>Deciduous forest</td>
<td>oak, beech, birch, poplar</td>
<td>0.5 - 10</td>
<td>0.05 – 0.5</td>
<td></td>
</tr>
</tbody>
</table>

*) 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

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 does not deserve high efforts. Instead, it is better to concentrate on sophisticated calculations for the critical leaching rate.

V.5.2.1.3 CRITICAL LEACHING OF HEAVY METALS FROM THE SOIL

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

\[ Q_{le} = M_{le(crit)} \times c_{le} \times \left[ \frac{M_{tot,sdw(crit)}}{Q_{le}} \right] \]

where:
\[ M_{le(crit)} = \text{critical leaching flux of heavy metal from the topsoil (g ha}^{-1} \text{ a}^{-1}) \text{ (see eq. V.88)} \]
\[ c_{le} = 10 \text{ g mg}^{-1} \text{ m}^2 \text{ ha}^{-1}, \text{ factor for appropriate conversion of flux units} \]
\[ Q_{le} = \text{flux of drainage water leaching from the regarded soil layer defined as above (m a}^{-1}) \]
\[ [M_{tot,sdw(crit)}] = \text{critical total concentration of heavy metal in the soil drainage water (mg m}^{-3}) \text{ (derived from critical limits, see V.5.2.2)} \]
V.5.2.1.3.1 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<sub>h</sub>, A<sub>p</sub>) 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<sub>le,zb</sub>) at steady state can be calculated according to:

\[
Q_{le,zb} = P - E_i - E_s - f_{Et,zb} \cdot E_t
\]

where:
- \(P\) = precipitation (m a<sup>-1</sup>)
- \(E_i\) = interception evaporation (m a<sup>-1</sup>)
- \(E_s\) = actual soil evaporation within the topsoil defined as above (m a<sup>-1</sup>)
- \(E_t\) = actual plant transpiration (m a<sup>-1</sup>)
- \(f_{Et,zb}\) = 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 \(Q_w\) 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:

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

where:
- \(P_m\) = annual mean precipitation (m a<sup>-1</sup>, data adjusted for common measurement bias)
- \(T_m\) = annual mean air temperature (°C)
- \(E_{m,pot}\) = annual mean potential evapotranspiration in humid areas at \(T_m = 0^\circ C\); \(E_{m,pot} \approx 0.35 \, m \, a^{-1}\) in forests, possibly less in other terrestrial ecosystems.
- \(f_{E,zb}\) = Fraction of total annual mean evapotranspiration above \(z_b\) (–); \(f_{E,zb} \approx 0.8\) for the organic top soil layer of forests.

For forested areas, this relationship is supported by data not only on river runoff but also on soil percolation (e.g. based on Michalzik et al. 2001), which together suggest that about 80% or more of the total evapotranspiration takes place above or within the organic top soil layer. Thus, the mean water flux from the organic top layer \((Q)\) can easily be estimated from annual means of precipitation \((P)\) and air temperature \((T)\), which are two traditional climate normals available in traditional climate maps (see Background document, De Vries et al, 2005):

In European forest regions, \(Q_{le,zb}\) is typically 0.1-0.6 m a<sup>-1</sup>, but may reach >2 m a<sup>-1</sup> in coastal mountain regions. The standard parameter uncertainty is on the order of ±0.1 m a<sup>-1</sup> (i.e. about ±30%) at the landscape scale. Depending on climate, \(Q_w\) 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 \(Q_w\) relative to \(P\) can become very low. With eq. 5.91b, \(Q_w\) almost never drops below 0.1 m<sup>-1</sup> in Europe (considering EMEP-50 km grid square means). For eq. 5.91a, a suggested minimum value is 5% of the precipitation. This seems a reasonable lower value since there are always periods during the year with downward percolation and a situation of no leaching hardly (or never) occurs on a yearly basis. The use of monthly water balances is not advocated as the effect of all seasonal variations is not included in the critical limits, since these represent annual or long-term means, in line with the critical load approach for acidity.
V.5.2.1.3.2 Critical total dissolved or total concentrations of heavy metals in soil drainage water

Information on the derivation of critical total dissolved concentrations of heavy metals in soil drainage water, $[M]_{\text{dis, sdw (crit)}}$, either directly, through transfer functions (plant soil solution) or through $[M]_{\text{free, sdw (crit)}}$ is given in the next section (V.5.2.2), with background information on used approaches in the Annexes 1-3. The critical total dissolved metal concentrations related to ecotoxicological effects in soils require some specific considerations. These critical total metal concentrations in soil solution are determined as the sum of the critical concentration of the free metal ion $M^{2+}$, $[M]_{\text{free, sdw (crit)}}$, and the metals bound to dissolved inorganic complexes $[M]_{\text{DIC, sdw}}$ such as $\text{MOH}^{+}$, $\text{HC}O_{3}^{-}$, $\text{MCl}^{+}$, and to dissolved organic matter, $[M]_{\text{DOM, sdw}}$, according to:

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

where:

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

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

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

where:

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

In the calculations, we suggest particulate fraction to be neglected to get comparable values of critical concentrations for the different effects pathways (see Section V.5.2.2.3). In this manual, the description of methods is adapted to the use of the critical total dissolved metal concentrations, $[M]_{\text{dis, sdw (crit)}}$, being equal to total metal concentrations in soil solution, implicitly assuming that the concentration of metals bound to suspended particulate matter is negligible ($[SPM]_{\text{sdw}} = 0$), i.e. $[M]_{\text{dis, sdw (crit)}}$ equals $[M]_{\text{tot, sdw (crit)}}$.

V.5.2.2 CRITICAL DISSOLVED METAL CONCENTRATIONS DERIVED FROM CRITICAL LIMITS IN TERRESTRIAL ECOSYSTEMS

Critical total concentrations of the heavy metals $\text{Cd}$, $\text{Pb}$ and $\text{Hg}$ in the soil solution, $[M]_{\text{dis, sdw (crit)}}$, depend on the target to be protected. These values have to be derived from critical limits (see Table V.15):

- Critical metal concentrations in ground water ($\text{Cd}$, $\text{Pb}$, $\text{Hg}$) in view of human health effects through intake of drinking water.
- Critical concentrations of free metal ions in soil solution ($\text{Cd}$, $\text{Pb}$) in view of ecotoxicological effects on soil microorganisms, plants and invertebrates.
Chapter V – Mapping critical loads on ecosystems

Critical metal contents in the soil ($\text{Hg}$) in view of ecotoxicological effects on soil micro-organisms and invertebrates in the forest humus layer.

The critical total dissolved concentration of a heavy metal in the soil drainage water ($[M]_{\text{dis,sdw(crit)}}$) includes both the free metal ions and the metals bound to dissolved inorganic and organic complexes (eq. V.92).

The derivation of the critical total dissolved concentrations to be applied in eq. V.90 is explained below.

V.5.2.2.1 CRITICAL DISSOLVED CONCENTRATIONS OF $\text{Cd}$, $\text{Pb}$ AND $\text{Hg}$ IN VIEW OF CRITICAL PLANT METAL CONTENTS

Starting from the idea to derive critical total $\text{Cd}$, $\text{Pb}$ and $\text{Hg}$ 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 $\text{Cd}$, $\text{Pb}$ and $\text{Hg}$. It shows that only for $\text{Cd}$ significant relationships ($R^2 > 0.5$) are available.

V.5.2.2.1.1 Cadmium

Starting with a critical $\text{Cd}$ 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 $\text{Cd}$ contents in wheat in the Netherlands to calculated soil solution concentrations, that were derived by using measured total soil contents and soil properties and application of a transfer function, relating total concentrations in solution to the soil metal content (Römkens et al. 2004). By applying such a function, regression relationships were derived for $\text{Cd}$ in plant (wheat grains) as a function of $\text{Cd}$ in soil solution and vice versa as described in Table V.18. The best estimate of a critical $\text{Cd}$ concentration might be the mean of both estimates.

The EU regulation (EG) No.466/2001 uses a limit for $\text{Cd}$ of 0.2 mg kg$^{-1}$ fresh weight in wheat grains. This limit was derived with the principle “As Low As Reasonably Achievable” (ALARA) and is therefore not based on effects. There are however many indications that from the viewpoint of protection of human health, the critical limit of 0.1 mg kg$^{-1}$ fresh weight, which was used in the EU before 2001, is more appropriate (for these arguments see De Vries et al. 2003, 2005, 2007a). Table V.18 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$^{-3}$).

Table V.18: Values for the intercept (Int) and the parameter a in the regression relationships relating $\text{Cd}$ in plant (wheat grains) as a function of $\text{Cd}$ 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 $\text{Cd}$ concentration when applying a critical $\text{Cd}$ 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).

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

1 $\log(\text{Cd plant}) = \text{Int} + a \times \log(\text{Cd soil solution})$

2 $\log(\text{Cd soil solution}) = \text{Int} + a \times \log(\text{Cd plant})$
A more sophisticated and consistent way would be to:

- first derive a critical “pseudo” total soil metal content, by applying soil – plant relationships in the inverse way (derive a critical total soil content from a critical plant content).
- then apply a transfer function relating “pseudo” total metal contents to reactive metal contents (Annex 1, eq. A1.3).
- followed by a transfer function relating the free ion metal activity in solution to the reactive metal content (Annex 1, eq. A1.4 or eq. A1.5).
- followed by a calculation of total concentrations from free metal ion activities with a chemical speciation model (i.e. the W6S-MTC2 model, Section V.5.2.2.3).

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

### V.5.2.2.1.2 Lead and mercury

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

Critical concentrations given here are those in use in 2004. Since the EU regulation No 466/2001 has been updated by the EU regulation No. 1881/2006. The relevance of using the new regulatory values is to be assessed within the WGE prior to a potential update of the values recommended here.

### V.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 V.15). 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 its chapter III.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:

<table>
<thead>
<tr>
<th>Element</th>
<th>Critical Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>10 mg m$^{-3}$</td>
</tr>
<tr>
<td>Cd</td>
<td>3 mg m$^{-3}$</td>
</tr>
<tr>
<td>Hg</td>
<td>1 mg m$^{-3}$ (for total mercury)</td>
</tr>
</tbody>
</table>

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

2011 WHO recommendations for drinking waters are 6 mg m$^{-3}$ for inorganic mercury (WHO 2011). As for updated EU regulations, these values may be included in the CLd methodology once discussed within the ICP M&M.
V.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 V.15). 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 \[M_{\text{dis,sdw(crit)}}\] from critical limits for free metal ion concentrations using a chemical speciation model.

V.5.2.2.3.1 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 by application of regressions given in Annex 10 of the background document (De Vries et al. 2005), assuming that the pH in soil solution equals pH_{sdw}. EU Risk Assessment procedures do not require the organic matter content of the soil to be specified for data to be accepted. However, such data were not usable for the calculation of critical free metal ion concentrations from critical soil metal contents, since the used transfer functions do require these data (see Annex 1) and were thus removed from the databases.

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

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

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

More information on the approach and the toxicity data is given in Lofts et al. (2004) and in De Vries et al. (2004). A summary can be found in the background document (De Vries et al. 2005).
V.5.2.2.3.2 Calculation of total dissolved metal concentrations from free metal ion concentrations

To calculate critical loads for soils from the critical limit functions, it is necessary to know the total concentration of metal in soil drainage water that corresponds to the free ion critical limit. In Annex 2, an overview is given of the calculation procedure using the WHAM model. Results thus obtained with this model for an assumed standard CO$_2$ pressure of 15 times the atmospheric pressure of 0.3 mbar (4.5 mbar) are given in Tables V.19 and V.20. WHAM includes also the fraction of suspended particulate matter, which strictly is not part of the soil solution. The total concentration is therefore related to soil drainage water. When [SPM]$_{sdw} =$ 0, the value of [M]$_{tot,sdw(crit)}$ equals that of [M]$_{dis,sdw(crit)}$ (see eq. V.93). For reasons of consistency with the other approaches (see eq V.92), in which the critical value refers to [M]$_{dis,sdw(crit)}$, it is advocated to apply the results with [SPM]$_{sdw} =$ 0. Furthermore, there are high uncertainties in the data on SPM in soil solution. Table V.19 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 V.20).

V.5.2.2.3.3 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 V.19 and V.20). In the following recommendations are provided, which status of soil conditions should be considered, when $M_{dis,sdw(crit)}$ is derived from critical limits for free metal ion concentrations, as presented in the tables V.19 and V.20.
Table V.19: Look-up table to derive values of the total critical Cd concentrations in soil drainage water \([\text{Cd}]_{\text{tot,sdw(crit)}}(\text{mg.m}^{-3})\), being \([\text{Cd}]_{\text{dis,sdw(crit)}}(\text{mg.m}^{-3})\) at SPM=0.

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Table V.20: Look-up table to derive values of the total critical Pb concentrations in soil drainage water \([\text{Pb}]_{\text{tot,sdw(crit)}}\) at a CO\(_2\) pressure that equals 15 times the CO\(_2\) pressure of the air \([\text{Pb}]_{\text{tot,sdw(crit)}}\) (mg.m\(^{-3}\)) at SPM=0

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<td>35.86</td>
<td>42.66</td>
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</table>
V.5.2.3.3.1 pH values

If possible, it is recommended to use the pH at steady state, assuming the implementation of the most recent regulations (such as the revised Gothenburg protocol). It may be necessary to run dynamic models to obtain this steady state pH value.

Alternatively, and pragmatically, the present soil solution pH may be used. It is then assumed that present pH is (almost) equal to future pH under most recent regulations. If the present pH in soil solution is not available, soil solution pH may be derived from pH in water or pH in salt extracts through regression functions. Linear relation coefficients are given in Table V.20 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.

A last approach, however not recommended, is to use the pH at the critical acid load. This pH is easier to calculate but may strongly deviate from pH at steady state. Furthermore, the calculation of the critical load pH is rather uncertain as it depends on arbitrary choices. These relations can be used to calculate the soil solution pH which is needed in the critical load calculations and also in the transfer functions relating reactive metal contents to free metal ion concentrations.

More detailed information is given in Annex 10 in the background document (De Vries et al. 2005). 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.

**Table V.21:** Results of linear regression analyses of the pH in soil solution against pH-H₂O, pH-CaCl₂ and pH-KCl. (pHsoil solution = α pH-X + β, with X = H₂O, CaCl₂ or KCl)

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<th>Intercept (β)²</th>
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<th>R²_adj⁴</th>
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¹) Number of samples
²) All coefficients are significant at p > 0.999
³) se_Yest: Standard error of estimated Y
⁴) R²_adj: Adjusted R²

V.5.2.2.3.3.2 DOC concentrations

The concentration of dissolved organic matter (DOM) in soils is nowadays frequently determined in climaterelated studies. Concentrations of DOM are usually determined by analysis of carbon (DOC) which accounts for half of the weight of soil organic matter (DOM = 2 × DOC). However, long-term data on soil solutions are rarely available at sufficient density for mapping region-specific means and variability’s, and may need to be estimated from studies elsewhere. Ranges in DOC values for major forest types and soil layers, by means of the 5-, 50- and 95 percentiles, are presented in Annex 11 of the background document (De Vries et al. 2005) 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. 2005) 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 (De Vries et al. 2005). The results show a good relationship with the site and soil characteristics in the subsoil (below 30cm) but the relationships were much worse in the topsoil (above 30cm). In the topsoil there was a clear positive relationship with C/N ratio and temperature, while the correlated values of the individual C and N concentrations were negatively and positively related to DOC, respectively. The relationships are, however, too weak to be very useful. This is in line with the limited number of studies in the literature, from which no significant relationship could be discerned (Michalzik et al. 2001).

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

Forest organic layer (O horizon):

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

Forest mineral topsoil (0-10 cm):

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

Grass land (0-10 cm):

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

Arable land (0-30 cm):

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

**V.5.2.2.4 CRITICAL DISSOLVED CONCENTRATIONS OF HG RELATED TO ECOTOXICOLOGICAL EFFECTS IN SOILS**

**V.5.2.2.4.1 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).
V.5.2.2.4.2 Transfer function for mercury

The critical leaching of Hg from the humus layer \((M_{le}(crit)}\) in eq. V.88) is related to the mobility and Hg content of dissolved organic matter because of the strong affinity of Hg for living and dead organic matter and the resulting lack of competition by inorganic ligands in this layer (e.g. Meili 1991, 1997). Because of the strong association of Hg with organic matter leaving virtually no free ions (apparently far less than one per km² of topsoil, based on Skyllberg et al. 2003), the biogeochemical turnover of Hg is controlled by the competition between biotic and other organic ligands. Therefore, Hg/OM ratios are a useful tool for calculating critical limits and loads and associated transfer functions (Meili et al. 2003a). This is the basis of the transfer function to derive total Hg concentrations in percolating (top)soil water \((\{M\}_{dis, sdw}(crit)}\) in eq. V.90, \(mg \ m^{-3}\) as follows:

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

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

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

V.5.2.2.4.3 Critical concentration for the soil drainage water:
Based on the Hg limit of 0.5 mg kg⁻¹ OM and a DOM concentration of 70 mg l⁻¹ \((DOC = 35 \ mg \ l^{-1})\), the critical steady state concentration of total Hg in soil drainage water is 35 ng l⁻¹ or 0.035 μg l⁻¹ (see eq. V.96). This concentration is consistent with that derived by a different approach at the watershed scale (Meili et al. 2003a) and is similar to high-end values presently observed in soil solutions and surface freshwaters (Meili, 1997; Meili et al. 2003b; Åkerblom et al. 2004). Note that this ecosystem limit for soil water is much lower than the drinking water limit above, but still higher than that for surface freshwaters where Hg limits for fish consumption usually are exceeded at surface water concentrations of 1-5 ng l⁻¹.

V.5.3 AQUATIC ECOSYSTEMS

V.5.3.1 CRITICAL LOADS OF CADMIUM AND LEAD

V.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 V.5.3.2.
V.5.3.1.1.1 Steady-state mass balance model in stream waters

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

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

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

(V.97)  

where:

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

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

\[ CL(M) = M_u + M_{lo(crit)} \]

(V.98)  

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

V.5.3.1.1.2 Heavy metal removal by net uptake

The assessment of these data is comparable for those in terrestrial ecosystems (see eq. V.89), but now the uptake or release refers to the complete catchment. This implies that no further reduction factors need to be applied to relate the uptake in the root zone/catchment to the mineral topsoil. The equation for net uptake is thus equal to eq. V.89 with \( f_{Mu} \) being equal to 1.

V.5.3.1.1.3 Critical output of heavy metals from the aquatic system

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

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

where:

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

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

$$\text{(V.100)}$$

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

where:

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

Data on the lateral outflow of lakes can be derived from the S&N critical loads database. The critical load depends on the critical limit used. In the initial manual for aquatic ecosystems (De Vries et al. 1998), it was argued that critical limits referring to the free metal ion activity in surface water are most appropriate. This idea has been further developed by Lofts et al. (unpublished data), but has not been adopted here, for reasons which will be given in V.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. 2005). Like for terrestrial ecosystems, it is recommendable to calculate weathering rates (here at least for a depth of 1 m) to account for the influence of natural processes in comparison to atmospheric deposition in order to evaluate critical loads and critical limits exceedances. Information on how to calculate weathering within the catchment is given in Annex 6 of the background document (De Vries et al. 2005).

### V.5.3.1.2 CRITICAL TOTAL DISSOLVED CADMIUM AND LEAD CONCENTRATIONS IN AQUATIC ECOSYSTEMS

#### V.5.3.1.2.1 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 V.5.2.2 for toxic effects on the soil ecosystem. However, although there is no theoretical reason why the sensitivities of soil and water organisms to metals should not be similar (assuming that uptake of the free ion from the aqueous phase is the significant mechanism leading to toxicity) this approach has not been adopted for the following reasons:

1. The aquatic toxicity data for Cd covered a more restricted $pH$ range than for the terrestrial toxicity data ($pH$ 6.9 to 8.7

compared to $pH$ 3.2 to 7.9). Therefore, although overlap of points was seen within the $pH$ range covered by the aquatic toxicity data, no data were available to validate the theory of overlap below $pH$ 6.9.

2. Observed overlapping of points for Pb was less than for any of the metals studied (Cu and Zn in addition to Cd and Pb). Most of the aquatic toxicity data gave free Pb endpoints higher than those observed for soils.

For these reasons, it was decided not to use the free ion approach for aquatic critical limits and instead to express the critical limits as the total dissolved metal (mg m$^{-3}$).

A summary of preliminary effect-based critical limits is given in Table 5.24. The values for Cd are based on the EU Risk...
Assessment Report for Cd (Risk assessment Cadmium metal CAS-No. 7440-43-9). The values for Pb are based on Crommentuijn et al. (1997) for the value suggested for use in the 2004 call for data, and on a substance data sheet on Pb and its compounds (2003) for the value to be used with the 2005 update of Annex 3. There are also critical limits related to secondary poisoning, but these values are not yet recommended for use because they do require further substantiation and discussion.

The value of 0.38 mg m\(^{-3}\), taken from EU Risk Assessment Report for Cd, is based on the 5-percentile cut-off value of chronic toxicity data from 168 reliable tests on single species and 9 multi-species studies. An assessment factor of 2 is further introduced in the report, leading to a critical limit of 0.19 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. Since 2004, it has been also accepted to take the influence of hardness on the toxicity of cadmium into account, using 3 hardness classes (with hardness \(H\) in mg CaCO\(_3\) 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, De Vries et al, 2005).

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).

### Table V.22: Recommended critical limits for dissolved Cd and Pb concentrations surface waters

<table>
<thead>
<tr>
<th>Metal</th>
<th>Critical dissolved concentration (mg m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Value used before 2005</td>
</tr>
<tr>
<td>Cd</td>
<td>0.38 (^{1})</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>11</td>
</tr>
</tbody>
</table>

\(^{1}\) 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 \(\mu\)g Cd /kg food (wet weight) of the predator, being the quality standard for biota tissue with respect to secondary poisoning. However, this value is yet considered too uncertain to be used in the critical load calculations.

\(^{2}\) \(H = \) hardness in mg CaCO\(_3\) l\(^{-1}\)
(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\(^{-1}\) 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 considered too 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.

### Regulation update:

The recommended values for use in this Manual are the ones that were agreed upon when the 2004 version of the Manual was prepared. Since then, new EU legislation (Directive 2013/39/UE) have been published. They are mentioned here for information. The values in the table below are not compatible with data used in the Annex 3 of this section.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Critical dissolved concentration (mg m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg.m(^{-3})</td>
</tr>
<tr>
<td>Cd</td>
<td>≤0.08</td>
</tr>
<tr>
<td></td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
</tr>
<tr>
<td>Pb</td>
<td>1.3(^2)</td>
</tr>
<tr>
<td>Hg</td>
<td>0.07(^3)</td>
</tr>
</tbody>
</table>

1 Annual Averages of Environmental Quality Standards for inland surface waters as in Directive 2013/39/EU 2013.

2 This Environmental Quality Standard applies to lead bioavailable fraction.

3 Maximum allowable concentrations for inland waters
V.5.3.1.2.2 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 ([\(M\)\(_{SPM}\)]) from total dissolved metal concentrations in surface water ([\(M\)\(_{tot,sw}\)]). The simplest approach is an 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 to the values given in Table V.22 (taking into account water hardness for Cd and 5 mg m\(^{-3}\) for Pb. Use of different values implies a rerun of the WHAM model.

V.5.3.1.2.3 Surface water chemistry data

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

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

When calculating in-lake retention in deriving critical loads for lakes, data on characteristics such as the lake and catchment area and the net retention rate are needed. For more information we refer to the background document (De Vries et al. 2005) and an earlier manual (De Vries et al. 1998).
V.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.

V.5.3.2.1 DERIVATION OF CRITICAL LEVELS OF MERCURY IN PRECIPITATION REFERRING TO A STANDARD FISH

V.5.3.2.1.1 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:

\[ \text{[Hg]}_{\text{Pike}} = c_{bp} \cdot \text{[Hg]}_{\text{Prec}} \cdot \text{TF}_{\text{HgSite}} \]

where:

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

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

\[ \text{[Hg]}_{\text{Prec(crit)}} = \left( \frac{\text{[Hg]}_{\text{Pike(crit)}}}{\text{TF}_{\text{HgSite}} \cdot c_{bp}} \right) \]

where:

- \( \text{[Hg]}_{\text{Pike(crit)}} = 0.3 \, \text{mg kg}^{-1} \), critical Hg concentration in the flesh of 1-kg pike.
- \( \text{[Hg]}_{\text{Prec(crit)}} = \text{critical Hg concentration in precipitation (ng l}^{-1}) \)
- \( c_{bp} = 10^{-6} \, \text{mg ng}^{-1} \), factor for appropriate conversion of flux units.

Regarding the critical limit for mercury in pike of 0.3 mg kg\(^{-1}\) fw, we refer to the background document of the manual (De Vries et al. 2005).

V.5.3.2.1.2 The transfer function \( \text{TF}_{\text{HgSite}} \)

\( \text{TF}_{\text{HgSite}} \) 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, \( \text{TF}_{\text{HgSite}} \) is preferably expressed as a function of basic physical chemical parameters. Hg concentrations in fish are generally highest in nutrient-poor softwaters in acidic watersheds rich in wetlands (e.g., Verta et al. 1986, Håkanson et al. 1988, Meili 1991a, 1994, 1996a, 1997). Such differences can be described by empirical relationships to address regional and local differences in watershed biogeochemistry, based on
variables for which data are commonly available (e.g. from other studies under CLRTAP), such as surface water pH or concentrations of organic carbon or nutrients (the latter being of particular relevance for mercury). Two alternative formulations capturing part of the large variation in $TF_{HgSite}$ are:

\[(V.103a)\]

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

\[(V.103b)\]

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

where:

- $[TOC]_{sw}$ = concentration of total organic carbon in surface water (mg l$^{-1}$)
- $[TP]_{sw}$ = concentration of total phosphorus in surface water (mg l$^{-1}$)
- $pH_{sw}$ = 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 (V.103a) 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 (V.103b) is less adequate but can be used if data access is limited.

$TF_{HgRun}$ can be quantified from adequate data sets in various ways (see Annex 13 of the background document, De Vries et al. 2005). If such data are not available, a value of 250 000 l kg$^{-1}$ fw can be used for $TF_{HgRun}$ referring to the standard fish (1 kg, in particular pike, *Esox lucius*) at steady state (Meili et al. 2003a, cf. Verta et al. 1986, Meili 1991a). An important aspect to consider when quantifying $TF_{HgRun}$ (or other steady state parameters) from field data is that present environmental Hg concentrations are not in steady state with the present level of atmospheric pollution.

**V.5.3.2.2 DERIVATION OF CRITICAL LEVELS OF MERCURY IN PRECIPITATION REFERRING TO OTHER ORGANISMS**

**V.5.3.2.2.1 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:

\[(V.104)\]

\[[Hg]_{Bio} = [Hg]_{Pike} \cdot TF_{HgBio}\]

where:

- $[Hg]_{Bio}$ = Hg concentration in any biota, e.g. fish flesh (mg kg$^{-1}$ fw)
- $TF_{HgBio}$ = organism-specific transfer function addressing the typical Hg partitioning within food webs (-)

The critical level of atmospheric pollution ([Hg]$_{Prec(crit)}$) can thus be calculated from a combination of eq. V.102 and eq. V.104 as follows:

\[(V.105)\]

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

where:

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

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

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

\[
TF_{HgBio} \approx f_{HY} + f_{HW} W^{2/3}
\]

where:

- \( f_{HY} \): value for very young fish and other small animals (–); \( f_{HY} \approx 0.13 \)
- \( f_{HW} \): species-specific slope coefficient (–); \( f_{HW} = 0.2...2 \) (Table 5.25)
- \( W \): total body fresh weight (kg fw)

For many freshwater fish used for human consumption, this will generate estimates of mean Hg concentrations at a given fish size that differ less than 2-fold from observed means. Species-specific slope coefficients \( f_{HW} \) for some common freshwater fish are given in Table V.23 for the typical case that the value for very young fish and other small animals \( f_{HY} \) 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 \( f_{HW} = 0.87 \) (Table V.23). If fish weight data are not available, total body weight \( W \) in kg can be estimated from total body length by applying a species-specific shape factor \( f_{LW} \) (Table V.23) according to:

\[
W \approx f_{LW} \cdot L^{3.1}
\]

where:

- \( L \): length of the fish (cm)

Table V.23: Coefficients for size conversion \( f_{LW} \) and normalization of Hg concentrations \( f_{HW} \) in freshwater fish, some standard fish weights \( W \) for consumption and the related value for \( TF_{HgBio} \)

<table>
<thead>
<tr>
<th>Fish taxa</th>
<th>( f_{LW} )</th>
<th>( f_{HW} )</th>
<th>( W )</th>
<th>( TF_{HgBio} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>pike</td>
<td>Esox lucius</td>
<td>3.8 ( 10^{-6} )</td>
<td>0.87</td>
<td>1.0</td>
</tr>
<tr>
<td>pike-perch, zander</td>
<td>Stizostedion lucioperca</td>
<td>6.4 ( 10^{-6} )</td>
<td>1.2</td>
<td>1.0</td>
</tr>
<tr>
<td>perch</td>
<td>Perca fluviatilis</td>
<td>7.9 ( 10^{-6} )</td>
<td>1.9</td>
<td>0.3</td>
</tr>
<tr>
<td>trout</td>
<td>Salmo trutta</td>
<td>7.2 ( 10^{-6} )</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Arctic char</td>
<td>Salvelinus alpinus</td>
<td>6.8 ( 10^{-6} )</td>
<td>0.7</td>
<td>0.3</td>
</tr>
<tr>
<td>whitefish</td>
<td>Coregonus spp.</td>
<td>6 ( 10^{-6} ) &lt;0.4...&gt;2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>burbot</td>
<td>Lota lota</td>
<td>5 ( 10^{-6} )</td>
<td>0.9</td>
<td>0.3</td>
</tr>
<tr>
<td>bream</td>
<td>Abramis brama</td>
<td>8 ( 10^{-6} )</td>
<td>0.25</td>
<td>0.3</td>
</tr>
<tr>
<td>roach</td>
<td>Rutilus rutilus</td>
<td>6.8 ( 10^{-6} )</td>
<td>0.6...1.2</td>
<td></td>
</tr>
</tbody>
</table>

Table V.23 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 \( TF_{HgBio} = 1 \).
V.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, may be remarkable in certain soils, this holds in particular for Pb. It was, however, not recommended to consider this, in order to be consistent with other parts of the manual,

- The seasonal variation of soil parameters such as pH, DOC cannot be accounted for in the models.
V.6 MODELLING CRITICAL LOADS FOR BIODIVERSITY

V.6.1 INTRODUCTION

The critical loads concept has been developed to give a measure of the good ecological state of an ecosystem on the long term in relation to air pollutants. Initially this indicator has been based on chemical characteristics of soils. To complete the approach with a more ecological one, empirical critical loads considered the effects of atmospheric pollution on specific functions of an ecosystem or its overall good condition.

At its 25th session in 2007, the Executive Body encouraged the Working Group on Effects “… to increase its work on quantifying effects indicators, in particular for biodiversity. These should also be linked to the integrated assessment modelling activities” (ECE/EB.AIR/91, para. 31). This has been confirmed in the Long-term Strategy of the Convention till 2020 which “set a vision for the next 10 years and beyond to address the remaining issues from existing activities and to meet emerging challenges with the aim of delivering a sustainable optimal long-term balance between the effects of air pollution, climate change, and biodiversity” (ECE/EB.AIR/2010/4, para 6a). This has been thus explained in the 2012-2014 call for data issued by the CCE (CCE, 2012).

Responding to this request from the EB in 2007, the ICP M&M embarked on developing methods and data for biodiversity indicators that can be used for policy support through integrated assessment modelling. Preliminary results were reported in the CCE status report as soon as 2008 (Hettelingh et al., 2008). Following this, ICP M&M, the CCE and M&M NFCs have continued their activity on biodiversity indicators as reported every years in CCE status reports (Hettelingh et al., 2009; Posch et al., 2011, 2012; Slootweg et al., 2010). This was a logical methodological evolution that aimed at linking critical loads to biodiversity. These new developments, based on recent scientific findings, are described in this section. Under the WGE, different ICPs have also undertaken to develop indicators linking atmospheric pollution to biodiversity changes, as shown in Harmens et al (2013).

The work undertaken under ICP M&M, and more widely by the WGE, meet general preoccupations about the observed loss of biodiversity at the world scale (cf. http://www2.epa.gov/nutrientpollution, http://www.initrogen.org, Sutton et al., 2011). Also, pollution deposition, in particular nitrogen, is included in the threats to biodiversity listed by the Convention on Biological Diversity (CBD, decisions VII/30 in 2004 and VIII/15 in 2006). Nitrogen deposition has been shown to be above critical loads for a significant number of protected areas across the world, indicating that nitrogen deposition is one of the drivers of biodiversity loss (Bleeker et al., 2011). Assessments for the revision of the Gothenburg protocol evaluated that, in 2005, over 57% of the EMEP area the critical loads for eutrophication were exceeded (WGE, 2013).

Published in 2010, the CBD “strategic plan for biodiversity 2011-2020” translated its decisions into the Aichi Targets (in particular “Target 8: By 2020, pollution, including from excess nutrients, has been brought to levels that are not detrimental to ecosystem function and biodiversity”). In 2011, its Subsidiary Body on Scientific, Technical and Technological Advice recommended that this target was supported by indicators expressing the trends in pressures from pollution such as “Trends in water quality in aquatic ecosystems”, “Trends in pollution deposition rate”, “Trends in emission to the environment of pollutants relevant for biodiversity”, “Trends in ozone levels in natural ecosystems” (Target 8, recommendation XV/1, CBD, 2011).

At European level, the pan-European initiative launched in January 2005 developed a set of indicators to assess progress towards CBD 2010 biodiversity target in Europe, the Streamlining European 2010 Biodiversity Indicators (SEBI 2010, http://biodiversity.europa.eu/topics/sebi-indicators). One of these indicators, in line with the Aichi target 8, is the critical load exceedance for nitrogen (SEBI 09).

The EU Biodiversity Strategy for 2020 (EC, 2011), adopted through a European
Parliament resolution in 2012, emphasizes the importance of the SEBI indicators for implementing and assessing policy efficiency. Its target 2, action 7, encourages member states to “Ensure no net loss of biodiversity and ecosystem services”.

For Europe, the EU specified six 2020-biodiversity targets. In particular for EU Member States, results of this work could contribute and support the EU 2020 headline target “halting the loss of biodiversity and the degradation of ecosystem services in the EU by 2010, and restoring them in so far as feasible, while stepping up the EU contribution to averting global biodiversity loss”. This objective has been abbreviated in the EU to “no net loss of biodiversity and ecosystem services” (EU, 2011, p.12, Target 2, Action 7) which was simplified to “no net loss of biodiversity” for the purpose of this Call. For more detailed background information, NFCs may wish to consult the documents listed in the CCE Call for Contributions of 2011-2012 (To be found at: http://wge-cce.org/Activities/Call_for_Data).

V.6.2 OBJECTIVES

In this context, ICP M&M and CCE have promoted the development of modelling tools based on biodiversity metrics (instead of a physico-chemical indicator) and integrating the effects of climate change. These tools may calculate nitrogen critical loads in relation to an acceptable plant species diversity changes or predict vegetation changes under different scenarios. Available approaches, used by ICP M&M NFCs, are briefly described below.

At the ICP M&M meeting and CCE workshop in 2012 in Warsaw, Poland,(see www.icpmapping.org for minutes), NFCs have furthermore been encouraged to choose indicators that may provide a measure of “no net loss of biodiversity” for sensitive plant species or ecosystems that are of relevance for individual countries. In this context an approach is adopted which is similar to previous calls for ICP M&M relative to critical loads data. The reason is that in their response to calls for critical loads data, countries are free to decide on the sensitive ecosystems for which they wish to include critical loads in the European critical load database. This way of harmonisation of information on impacts provides a level playing field for the comparison, by policy analysts, of impacts generated from emission reduction scenarios that are simulated in integrated assessment.

In this way, the use of future “no net loss of biodiversity” indicators in integrated assessment models becomes similar to the manner in which the European critical loads database is implemented and used in effect based scenario analysis.

Following the 2012-2014 call for data, the ICP M&M discussions concluded that a common indicator, preliminarily named “habitat suitability indicator”, should be used by all NFCs, in addition to indicators that meet specific national requirements. This indicator should be calculated using lists of species characteristic of EUNIS habitats.

The most recent information on the development of “no net loss of biodiversity indicators” and “habitat suitability indicators” is to be found on the ICP M&M and CCE websites. These indicators are to be calculated from a number of tools and models that are made available through the CCE for NFCs to carry out their calculations. NFCs are encouraged to make use of them especially when they do not have at their disposal more accurate or detailed national tools equivalent to the ones listed here. These tools and models are briefly described in the following sections. Further information is to be found in the CCE Status Reports, in particular the 2009 and 2014 reports, and in the Minutes from ICP M&M Task Force and CCE Workshop meeting in 2014.

**V.6.3 THE DATABASES**

**V.6.3.1 THE HARMONISED LAND COVER MAP**

This map provides information on the vegetation type on a 100 x 100 m² grid. It has been compiled by the Stockholm Environment Institute from existing digital and paper sources including the European Environment Agency (EEA) Corine Land Cover 2000, SEI Land European Cover Map (2002 Revision), FAO Soil Map of the World, EEA European Biogeographical regions (2005). Vegetation types are identified by their EUNIS Code (cf. [http://eunis.eea.europa.eu/](http://eunis.eea.europa.eu/)). The map dataset contains information down to EUNIS level 3 for specific habitat types. For more detailed information, please refer to Cinderby et al., 2007, Slootweg et al., 2009.

The harmonised land cover map is available in a format compatible with the EMEP grid from the CCE.

**V.6.3.2 THE EU BACKGROUND DATABASE**

The European background database (EU DB) has been developed by the CCE in order to test new methods, to fill gaps of the European wide critical maps and to carry out dynamic modelling). Over the years, the CCE has maintained and updated the EU DB with information provided by parties, especially following calls for data. Detailed information is to be found in De Smet and Heuvelmans, 1997, Posch and Reinds, 2005, Reinds, 2007, Slootweg et al., 2008, Slootweg et al., 2009 and Slootweg et al., 2011.

The European background database (EU DB) includes the latest available data on a European scale for the calculation of critical loads and for running simple dynamic models. Different ecosystem types are included, identified by their EUNIS code (Marine habitats (A), Coastal habitats (B), Inland surface water habitats (C), Mire, bog and fen habitats (D), Grassland and tall forb habitats (E), Heathland, scrub and tundra habitats (F), Woodland and forests habitats (G)). Forests soils are considered with a distinction between coniferous, broad leave deciduous and mixed forests (EUNIS level 2 and 3). The EU-DB includes parameters describing climatic variables, base cation deposition and weathering, nutrient uptake, nitrogen transformations and cation exchange. It includes a map combining land use, soil characteristics, average forest growth (reference year 2005), altitude, and the 5x5 km² EMEP grid. Using the Simple Mass Balance model, critical loads were calculated over the EMEP grid.

In 2013, the WGE “requested that the European Background Database would be used by the CCE for effect-based assessments, after CCE have checked with National Focal Centres (NFCs) that national data are not available, unless countries request the CCE not to carry out calculations for a given parameter on their national territory” (ECE/EB.AIR/WG.1/2013/2).

**V.6.4 VEGETATION MODELS MAY BE USED TO PREDICT BIODIVERSITY CHANGES**

In the present context, vegetation models simulate vegetation developments or changes in relation to abiotic conditions (nutrients, basic cations, light or water availability, soil acidity, temperature...). These conditions are provided by models such as VSD+ (see chapter VI).

Vegetation models have been developed and tested under ICP M&M for several years (see for instance De Vries et al., 2010 for a comparison of 4 of them). In the following sections, some of these approaches are presented. Models are sorted in alphabetical order. Further details on the models are to be found in the bibliographic references and in particular in De Vries et al (in press - 2014).
V.6.4.1 BERN
The BERN model simulates the potential plant community composition depending on the geo-chemical soils characteristics and climatic conditions. It uses fuzzy functions for 7 different factors (soil water content, base saturation or pH, C:N ratio, climatic water balance, vegetation period, solar radiation and temperature). These functions represent the ecological niche under pristine or semi-natural conditions (Schlutow and Huebener, 2002, Nagel et al., 2012).

V.6.4.2 GROWUP
The GrowUp model simulates forest growth, nutrient uptake and litterfall. This model includes the effects of forest management (Bonten et al., 2013).

V.6.4.3 MOVE
The MOVE model assesses changes in plant species occurrence due to changes in abiotic site conditions. This statistical model is based on response curves that define probability of occurrence of plant species along environmental gradients (de Vries et al., 2007; Latour and Reiling, 1993; Latour et al., 1994; Van Dobben et al., 2010).

V.6.4.4 PROPS
The PROPS model estimates the probability of plant species occurrence as a function of environmental factors. It is associated to a database including over 40 000 vegetation relevés. At some of the sites soil parameters such as pH and C/N ratio have been measured as well. The PROPS model has been coupled to the biogeochemical model VSD+ (Reinds et al., 2013).

V.6.4.5 SUMO
In SUMO, the biomass development of five functional plant types is simulated as a function of nitrogen availability, light interception and management. This process-based model simulates the change in biomass distribution over functional types during the succession from almost bare soil via grassland or heathland to various forest types (Wamelink et al., 2009). The SUMO model has been coupled with the biogeochemical model SMART2 (Wamelink et al., 2009).

V.6.4.6 VEG
The Veg model estimates the composition of the ground vegetation community using abiotic conditions at a particular sites (Reinds et al., 2013). The composition of the ground vegetation community is simulated in the Veg module by distributing the available ground area (a hypothetical representative 1m2) over the plant species that would be able to establish at the site, given its abiotic conditions. For each species, a ‘niche window’ is estimated by the model. This niche window is the combined limits of N and Bc concentrations in the soil solution, soil solution pH, soil moisture, air temperature, and light intensity reaching the ground vegetation (light below tree canopy in case trees are present), within which a species could become established at a certain site. Usually, site conditions are favourable enough for several species to be present simultaneously. The model then calculates the relative ground area occupied by each species, depending on their vigour in response to site conditions and their respective competitiveness. The plant species compete by growing roots to different soil depths, and by shading other plants above ground. The root depth and shading eight are given as inputs for each indicator plant species (Belyazid et al., 2009;
The model requires a list of indicator plant species, which is typically based on input from biologists and ecologists familiar with the ecosystem to be modelled, the “Veg Table”. It contains information on plant species present in the different EUNIS classes. Initially compiled on the basis of Northern Europe plant relevés (Sverdrup et al., 2007), this table has been enriched or adapted by different countries. It thus progressively adapts to different European eco-regions (cf. for instance Braun et al., 2012; Nagel et al., 2012; Probst et al., 2012; Probst et al., 2014).

The Veg model has been coupled with the biogeochemical ForSafe and VSD+ models.

### V.7 REFERENCES


Achermann, B., and Bobbink, R., Swiss Agency for the Environment, Forests and Landscape (SAEFL), Bern, Switzerland. pp. 1-327.


Eurosoil (1999) Metadata: Soil Geographical Data Base of Europe v.3.2.8.0. Joint Research Centre, Ispra, Italy.


Chapter V – Mapping critical loads on ecosystems


Johnson DW, Cole DW, Gessel SP (1979) Acid precipitation and soil sulfate adsorption properties in a tropical and in a temperate forest soil. Biotropica 11: 38-42.


Chapter V – Mapping critical loads on ecosystems


V.8 ANNEXES

V.8.1 ANNEX 1: TRANSFER FUNCTIONS FOR LEAD AND CADMIUM FOR THE CONVERSION OF METAL CONCENTRATIONS IN DIFFERENT SOIL PHASES

Need of transfer functions in deriving critical dissolved metal concentrations

In principle, transfer functions are not needed in performing a critical load calculation. Transfer functions have been used to derive critical limits for free metal ion concentrations from NOEC data, referring to reactive soil metal contents. When applying critical limits for free metal ion concentrations, related to ecotoxicological effects, no transfer function is needed any more, since \([M]_{\text{soil crit}}\) can be obtained directly, either by reference to the look up tables or by use of the W6S-MTC2 program (see Section V.5.2.2.3). In case of ground water protection, total dissolved critical concentrations can be used directly (see Section V.5.2.2.2). In the case of using critical limits referring to the metal content in plants, an empirical relationship can be used to derive total dissolved critical concentrations in soil solution, at least for \(Cd\) (See Table IV). Using the more sophisticated and consistent way to derive soil solution concentrations from critical plant contents does however require transfer functions according to the following:

1. 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).
2. Then apply a transfer function relating pseudo-total metal contents to reactive metal contents (Annex 1, eq. A1.3).
3. Followed by a transfer function relating the free ion metal activity in solution to the reactive metal content (Annex 1, eq. A1.4 or eq. A1.5).

Furthermore, all the transfer functions listed below are needed for the calculation of a critical soil limit (from a given critical limit function for the soil solution) and to compare this to the present soil metal content to assess the critical limit exceedance in the present situation. This requires a map of the present soil metal content in the country. Inversely, one may calculate the present dissolved metal concentration from the present soil metal content, using the transfer functions described below and compare this to the critical limit function for the soil solution (see section V.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 \([M]_{\text{AR}}\)) from total contents (here \([M]_{\text{HF}}\), according to:

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

where:

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

\([M]_{\text{HF}} = \text{total content of heavy metal } M \text{ in soil, provided as HF-extraction (mg kg}\(^{-1}\))\]

Values for \(a_0\) and \(a_1\) are given in Tables A1.1 and A1.2. The correlations are depending on metal and substrate. In general, total and pseudo-total contents are very similar. For back-calculations of total contents from pseudo-total contents, different functions are to be used (see background document, De Vries et al 2005, Annex 7). These functions are not provided here, since those calculations are not needed in the present calculation of critical loads.
### Table A1.1: Relationship between cadmium (Cd) content in soils extractable by aqua regia (AR) and total contents in dependence on the parent material.

<table>
<thead>
<tr>
<th>Parent material</th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$n$</th>
<th>$R^2$</th>
<th>range of validity Cd (HF) (mg kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>basic and intermediate igneous rock</td>
<td>0.13</td>
<td>1.41</td>
<td>25</td>
<td>0.94</td>
<td>0.25, 1.12</td>
</tr>
<tr>
<td>boulder clay</td>
<td>0.09</td>
<td>1.38</td>
<td>26</td>
<td>0.91</td>
<td>0.07, 0.39</td>
</tr>
<tr>
<td>limestone</td>
<td>-0.15</td>
<td>1.24</td>
<td>25</td>
<td>0.91</td>
<td>0.26, 1.86</td>
</tr>
<tr>
<td>loess or loessic loam</td>
<td>-0.15</td>
<td>1.26</td>
<td>25</td>
<td>0.91</td>
<td>0.07, 0.88</td>
</tr>
<tr>
<td>marl stone</td>
<td>-0.05</td>
<td>1.24</td>
<td>25</td>
<td>0.93</td>
<td>0.10, 0.98</td>
</tr>
<tr>
<td>sand</td>
<td>-0.02</td>
<td>1.26</td>
<td>37</td>
<td>0.89</td>
<td>0.04, 0.65</td>
</tr>
<tr>
<td>sandy loess</td>
<td>0.29</td>
<td>1.78</td>
<td>36</td>
<td>0.82</td>
<td>0.06, 0.29</td>
</tr>
<tr>
<td>acid igneous and metamorphic rock</td>
<td>-0.09</td>
<td>1.08</td>
<td>25</td>
<td>0.80</td>
<td>0.09, 0.63</td>
</tr>
<tr>
<td>quartzitic sand stones and conglomerates</td>
<td>-0.11</td>
<td>1.23</td>
<td>25</td>
<td>0.81</td>
<td>0.07, 0.60</td>
</tr>
<tr>
<td>clay stone, hard argillaceous and silty slates</td>
<td>-0.05</td>
<td>1.33</td>
<td>25</td>
<td>0.96</td>
<td>0.14, 1.88</td>
</tr>
<tr>
<td>all parent materials</td>
<td>-0.12</td>
<td>1.19</td>
<td>274</td>
<td>0.91</td>
<td>0.04, 1.88</td>
</tr>
</tbody>
</table>

### 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.

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

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

Regression relations were derived from a Dutch dataset containing 630 soil samples which were both extracted with 0.43 Mol l\(^{-1}\) 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: Relationship between lead (Pb) content in soils extractable by aqua regia (AR) and total contents extractable by HF in dependence on the parent material.

<table>
<thead>
<tr>
<th>Metal</th>
<th>(\beta_0)</th>
<th>(\beta_1)</th>
<th>(\beta_2)</th>
<th>(\beta_3)</th>
<th>(R^2)</th>
<th>se-yest(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0.225</td>
<td>1.075</td>
<td>0.006</td>
<td>-0.020</td>
<td>0.82</td>
<td>0.26</td>
</tr>
<tr>
<td>Pb</td>
<td>0.063</td>
<td>1.042</td>
<td>0.024</td>
<td>-0.122</td>
<td>0.88</td>
<td>0.17</td>
</tr>
</tbody>
</table>

\(^1\) 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 is the whole range of critical receptor concentrations observed. This is relevant since the derived critical limit functions are dependent upon the transfer functions.

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

- Sauvé et al. (1998). Soil metal and labile Pb in Pb-contaminated soils of various origins. Free Pb concentrations were estimated by measurement of labile Pb using differential pulse anodic stripping voltammetry (DPASV) and speciation calculations.
- Sauvé et al. (2000). Soil metal and labile Cd in Cd-contaminated soils of various origins. Free Cd concentrations were estimated by measurement of labile Cd using differential pulse anodic stripping voltammetry (DPASV) and speciation calculations.
- Weng et al. (2002). Soil metal and free ion concentrations in sandy Dutch soils. Free Cd and Pb concentrations were estimated by the Donnan membrane technique.
- Tipping et al. (2003a). Soil metal and free ion concentrations in UK upland soils. Free Cd and Pb were estimated by using the WHAM6 speciation model (Tipping, 1998) to speciate the soil solution.

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

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

where:

- \([M]_{free,sdw}\) = the free metal ion concentration (mol l\(^{-1}\))
- \([M]_{re}\) = the reactive metal content in the solid phase (mol l\(^{-1}\))
- \([OM]_s\) = organic matter (%)
- \(pH_{sdw}\) = soil drainage water pH

Calculated values of the parameters are given in Table A1.4.
Table A1.4: Values for the regression coefficients for the free ion concentration - reactive metal content relationship (eq. A1.4) and statistical measures $R^2$ and 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.

<table>
<thead>
<tr>
<th>Metal</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>m</th>
<th>$R^2$</th>
<th>se(Y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>-0.08</td>
<td>-0.60</td>
<td>-0.53</td>
<td>0.60</td>
<td>0.624</td>
<td>0.53</td>
</tr>
<tr>
<td>Pb</td>
<td>4.32</td>
<td>-0.69</td>
<td>-1.02</td>
<td>1.05</td>
<td>0.854</td>
<td>0.60</td>
</tr>
</tbody>
</table>

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:

$$\log_{10}[M]_s = a + b \cdot \log_{10}[OM]_s + c \cdot pH_{sw} + m \cdot \log_{10}[M]_{free,sw} \quad (A1.5)$$

where

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

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

Use of transfer functions in the manual

The direct transfer function for the calculation of the free ion concentration from the soil reactive metal content (the c-Q relation) is used for the calculation of the $pH$-dependent critical limit functions (see Section V.5.2.2.3), in order to express the endpoint metal dose in toxicity experiments as the free ion concentration. The transfer function for the calculation of the soil reactive metal content from the free metal ion concentration (the Q-c relation) is used to calculate the critical SPM-bound metal ($[M]_{SPM \ (crit)}$) in surface waters (see Section V.5.2.2.3 and Annex 2).

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.

<table>
<thead>
<tr>
<th>Metal</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>m</th>
<th>$R^2$</th>
<th>se(Y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>-6.42</td>
<td>0.64</td>
<td>0.45</td>
<td>0.58</td>
<td>0.507</td>
<td>0.52</td>
</tr>
<tr>
<td>Pb</td>
<td>-5.42</td>
<td>0.55</td>
<td>0.70</td>
<td>0.61</td>
<td>0.698</td>
<td>0.45</td>
</tr>
</tbody>
</table>
V.8.2 ANNEX 2: CALCULATION OF TOTAL METAL CONCENTRATION FROM FREE METAL ION CONCENTRATIONS USING THE WHAM MODEL

The metal in soil drainage water comprises the following metal species:

<table>
<thead>
<tr>
<th>Metal species</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal free ion M(^{2+})</td>
<td>([M]_{\text{free,sdw}})</td>
</tr>
<tr>
<td>Inorganic complexes (\text{MOH}^+), (\text{MHCO}_3), (\text{MC}l^-) etc</td>
<td>([M]_{\text{DIC,sdw}})</td>
</tr>
<tr>
<td>Metal bound to (\text{DOM})</td>
<td>([M]_{\text{DOM,sdw}})</td>
</tr>
<tr>
<td>Metal bound to (\text{SPM})</td>
<td>([M]_{\text{SPM,sdw}})</td>
</tr>
</tbody>
</table>

Here, \(\text{DOM}\) is dissolved organic matter, and \(\text{SPM}\) is suspended particulate matter. The total concentration of metal in soil drainage water does not refer simply to dissolved components \((\text{\([M]_{\text{free,sdw}}\), \([M]_{\text{DIC,sdw}}\), and \([M]_{\text{DOM,sdw}}\})\) but also includes \([M]_{\text{SPM,sdw}}\). Data on \(\text{SPM}\) concentration in soil drainage waters may be scarce, and in many cases the contribution of \(\text{SPM}\) 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 \(\text{pH}\) and competitive effects due to major cationic species of \(\text{Mg, Al, Ca and Fe}\). 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. 2005). NFCs may calculate critical dissolved metal concentrations from the free ion concentration by one of three methods:

1. Linear interpolation in the look-up tables (chapter V.5.2.2.3). The look-up tables list critical dissolved metal concentrations (calculated using W6S-MTC2) for various combinations of \(\text{pH}\), concentrations of soil organic matter, dissolved organic carbon \((\text{[DOC]_{\text{sdw}}})\) and partial \(\text{CO}_2\) pressure \((\text{pCO}_2)\).

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 \(\text{[M]_{\text{tot,sdw(crit)}}}\) 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:

<table>
<thead>
<tr>
<th>code</th>
<th>(\text{pH})</th>
<th>% OM</th>
<th>(\text{pCO}_2)</th>
<th>DOC</th>
<th>SPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>code: the user’s identifier of the site</td>
<td>(\text{pH}): soil solution pH</td>
<td>% OM: the soil organic matter content</td>
<td>(\text{pCO}_2): the soil (\text{pCO}_2) expressed as a multiple of the atmospheric value</td>
<td>DOC: concentration of dissolved organic carbon in mg l(^{-1})</td>
<td>SPM: concentration of suspended particulate matter in mg l(^{-1})</td>
</tr>
</tbody>
</table>
Chapter V – Mapping critical loads on ecosystems

- Please see the background document (Annex 8 and 9) regarding the selection of
  pH and pCO₂ values. If data on DOC concentration are not available, a standard
  value of 20 mg l⁻¹ will be assumed.
- If data on pCO₂ are not available, a value of 15 x atmospheric will be assumed.
- If data on SPM are not available, a value of zero will be assumed.

Please note that it is necessary to recalculate values of soil pH (measured in
KCl, 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 critical
total Cd and Pb concentrations in surface water related to ecotoxicological effects

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

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

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

Step 1

The critical free metal ion concentrations ([M]ₗₚₑₑₜ, crit) (mol l⁻¹) are calculated using
WHAM6, for waters of different pH, DOC and pCO₂, making the same assumptions as are
used for calculating total metal from free-ion critical limits (for the Look Up Tables, see
5.5.2.2.3). These assumptions also lead to hardness values (H = hardness in mg
CaCO₃ l⁻¹). In the calculations the critical dissolved concentrations used depend on
the water hardness in case of Cd (0.16 mg m⁻³ if H < 100, 0.30 mg m⁻³ if 100 < H < 200
and 0.50 mg m⁻³ if H >200), whereas a value of 5 mg m⁻³ was used for Pb. Note that, here,
all waters are assumed to be “normal” with respect to dissolved Al (i.e. acid bog-waters
are not included).

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

\[
\log [M]_{\text{free,crit}} = A \cdot [DOC] + B \cdot pCO₂ + C
\]

where [DOC] is in mg l⁻¹ and pCO₂ is a multiple of the atmospheric pCO₂. Root
mean square errors in \(\log [M]_{\text{free,crit}}\) between the WHAM6 values and the
regression values are < 0.12 for Cd and < 0.18 for Pb. The regression coefficients are
given in Tables A3.1 and A3.2. Linear interpolation can be performed to obtain
coefficients for intermediate pH values.

<table>
<thead>
<tr>
<th>pH</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>-0.0004</td>
<td>0.0000</td>
<td>-8.87</td>
</tr>
<tr>
<td>5</td>
<td>-0.0053</td>
<td>-0.0001</td>
<td>-8.87</td>
</tr>
<tr>
<td>6</td>
<td>-0.0258</td>
<td>0.0040</td>
<td>-8.93</td>
</tr>
<tr>
<td>7</td>
<td>-0.0344</td>
<td>0.0189</td>
<td>-9.05</td>
</tr>
<tr>
<td>8</td>
<td>-0.0196</td>
<td>0.0466</td>
<td>-9.18</td>
</tr>
<tr>
<td>9</td>
<td>-0.0010</td>
<td>-0.0742</td>
<td>-9.44</td>
</tr>
</tbody>
</table>
### Table A3.2 Regression coefficients for estimating critical free Pb$^{2+}$ concentrations

<table>
<thead>
<tr>
<th>pH</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>-0.0020</td>
<td>0.0000</td>
<td>-7.66</td>
</tr>
<tr>
<td>5</td>
<td>-0.0231</td>
<td>0.0000</td>
<td>-7.70</td>
</tr>
<tr>
<td>6</td>
<td>-0.0546</td>
<td>0.0062</td>
<td>-8.19</td>
</tr>
<tr>
<td>7</td>
<td>-0.0681</td>
<td>0.0261</td>
<td>-9.33</td>
</tr>
<tr>
<td>8</td>
<td>-0.0641</td>
<td>0.0349</td>
<td>-10.33</td>
</tr>
<tr>
<td>9</td>
<td>-0.0160</td>
<td>-0.1303</td>
<td>-11.41</td>
</tr>
</tbody>
</table>

**Step 2**

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

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

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

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

**Step 3**

Using the assumptions about water composition (see Step 1), water hardness (mg CaCO$_3$ l$^{-1}$) is given by regression equations of the following form:

\[
\text{hardness} = A \cdot [\text{DOC}] + B \cdot \text{pCO}_2 + C \quad (A 3.3)
\]

where $[\text{DOC}]$ is in mg l$^{-1}$ and $\text{pCO}_2$ is a multiple of the atmospheric $\text{pCO}_2$. The regression coefficients are given in Table A3.3. Linear interpolation can be performed to obtain coefficients for intermediate pH values.

**Step 4**

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

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

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

pH = 6
DOC = 8 mg l\(^{-1}\)
pCO\(_2\) = 4 times atmospheric
SPM = 50 mg l\(^{-1}\)
% OM = 20

Step 1
Log \([Cd]_{\text{free(crit)}}\) = \((-0.0258 \cdot 8) + (0.0040 \cdot 4) + (-8.93)\)
= -0.206 + 0.016 - 8.93
= -9.12

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

Step 2
log \([Cd]_{\text{SPM (crit)}}\) = -6.42 + (0.45 \cdot 6) + (0.64 \cdot 1.30) + (0.58 \cdot -9.12) = -6.42 + 2.70 + 0.832 - 5.29 = -8.178

\([Cd]_{\text{SPM (crit)}}\) = 6.64 \cdot 10^{-9} (mol g\(^{-1}\)) \cdot 112 \cdot 10^6 = 7.43 mg kg\(^{-1}\)

log \([Pb]_{\text{SPM (crit)}}\) = -5.42 + (0.70 \cdot 6) + (0.55 \cdot 1.30) + (0.61 \cdot -8.60) = -5.42 + 4.20 + 0.715 - 5.25 = -5.755

\([Pb]_{\text{SPM (crit)}}\) = 1.76 \cdot 10^{-6} (mol g\(^{-1}\)) \cdot 207 \cdot 10^6 = 364 mg kg\(^{-1}\)

Step 3
HARDNESS = (0.23 \cdot 8) + (0.34 \cdot 4) + (-0.14)
= 1.84 + 1.36 - 0.14 = 3.1

Therefore

\([Cd]_{\text{sw(crit)}}\) = 0.16 µg l\(^{-1}\)
\([Pb]_{\text{sw(crit)}}\) = 5 µg l\(^{-1}\)

Step 4
\([Cd]_{\text{tot, sw(crit)}}\) = 0.16 + [(50 / 1000) \cdot 7.43)] µg l\(^{-1}\)
= 0.53 µg l\(^{-1}\)

\([Pb]_{\text{tot, sw(crit)}}\) = 5 + [(50 / 1000) \cdot 364)] µg l\(^{-1}\)
= 23 µg l\(^{-1}\)
FULL CALCULATION EXAMPLE #2

\[
pH = 8
\]

\[
DOC = 1 \text{ mg l}^{-1}
\]

\[
pCO2 = 10 \text{ times atmospheric}
\]

\[
SPM = 10 \text{ mg l}^{-1}
\]

\[
\% \text{ OM} = 20
\]

Step 1

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

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

Step 2

\[
\log [\text{Cd}]_{\text{SPM}}(\text{crit}) = -6.42 + (0.45 \cdot 8) + (0.64 \cdot 1.30) + (0.58 \cdot -8.73) = -6.42 + 3.60 + 0.832 - 5.06 = -7.048
\]

\[
[\text{Cd}]_{\text{SPM}}(\text{crit}) = 8.95 \cdot 10^{-8} \text{ mol g}^{-1} \cdot 112 \cdot 10^6 = 10.0 \text{ mg kg}^{-1}
\]

\[
\log [\text{Pb}]_{\text{SPM}}(\text{crit}) = -5.42 + (0.70 \cdot 8) + (0.55 \cdot 1.30) + (0.61 \cdot -10.05) = -5.42 + 5.60 + 0.715 - 6.13 = -5.235
\]

\[
[\text{Pb}]_{\text{SPM}}(\text{crit}) = 5.82 \cdot 10^{-6} \text{ mol g}^{-1} \cdot 207 \cdot 10^6 = 1205 \text{ mg kg}^{-1}
\]

Step 3

\[
\text{HARDNESS} = (0.36 \cdot 1) + (38.2 \cdot 10) + (-6.84) = 0.36 + 382 - 6.84 = 376
\]

Therefore

\[
[\text{Cd}]_{\text{sw}}(\text{crit}) = 0.50 \mu g l^{-1}
\]

\[
[\text{Pb}]_{\text{sw}}(\text{crit}) = 5 \mu g l^{-1}
\]

Step 4

\[
[\text{Cd}]_{\text{tot, sw}}(\text{crit}) = 0.50 + [(10/1000) \cdot 10] \mu g l^{-1} = 0.60 \mu g l^{-1}
\]

\[
[\text{Pb}]_{\text{tot, sw}}(\text{crit}) = 5 + [(10 / 1000) \cdot 1205] \mu g l^{-1} = 17 \mu g l^{-1}
\]