

Chapter 2

Geochemical Indicators for Use in the Computation of Critical Loads and Dynamic Risk Assessments

Wim de Vries, Maximilian Posch, Harald U. Sverdrup, Thorjörn Larssen, Heleen A. de Wit, Roland Bobbink and Jean-Paul Hettelingh

2.1 Introduction

To assess critical atmospheric deposition levels (critical loads) of acidity, nitrogen (N) and metals, an endpoint needs to be identified, such as tree growth, crop quality, plant species diversity and soil biodiversity. An endpoint can be defined as a 'specified sensitive element of the environment' that one wants to protect. To quantify impacts, a certain endpoint indicator is needed, which can be defined as 'a quantifiable measure describing the status of an endpoint'. In case of geochemical indicators, this is also called a chemical criterion. Finally, to assess (potential) risk, a critical limit is needed, which can be defined as a maximum or minimum value allowed for an endpoint indicator or chemical criterion. For example, an endpoint for N impacts is 'vegetation change', the 'endpoint indicator' or 'chemical criterion' is the dissolved N concentration and its critical limit is in the range 2.5–6.0 mg N l⁻¹.

With respect to the assessment of critical loads, a distinction can be made between an empirical approach and a model-based approach. In the empirical approach, critical loads are derived from observed relationships between atmospheric deposition and effects on 'specified sensitive elements' within an ecosystem (ecosystem status) by correlative or experimental research. Such an approach has, for example, been used for nitrogen in view of adverse impacts on biodiversity, since N has a dominat-

W. de Vries (✉)

Alterra Wageningen University and Research Centre, Wageningen, The Netherlands
e-mail: wim.devries@wur.nl

M. Posch · J.-P. Hettelingh

Coordination Centre for Effects (CCE), RIVM, Bilthoven, The Netherlands

H. U. Sverdrup

Department of Chemical Engineering, Lund University, Lund, Sweden

T. Larssen · H. A. de Wit

Norwegian Institute for Water Research, Oslo, Norway

R. Bobbink

B-Ware Research Centre, Radboud University Nijmegen, Nijmegen, The Netherlands

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ing influence on species diversity of terrestrial vegetation. Details on this approach are given in Chaps. 4 and 5. Tables with empirical critical N load values and estimates of their reliability have been compiled since the beginning of the nineties (Bobbink et al. 1992), followed by an updated background paper (Bobbink et al. 1996), published as Annex III in the 1996 Mapping Manual (UBA 1996), followed by an extensive review and update in the period 2001–2002 (Achermann and Bobbink 2003) and recently updated (Bobbink and Hettelingh 2011), and now included in the Mapping Manual (www.icpmapping.org).

One of the drawbacks of empirical critical (nitrogen) loads is that the endpoints which they aim to protect vary between ecosystems. Moreover, they are generally based on comparatively short-term experiments and thus provide limited knowledge of the evolution of impacts over time. Finally, the variation in critical loads for a given ecosystem is not spatially explicit but only included by expressing the critical load as a range. An alternative approach is thus to use models that enable the assessment over time and space of the risk of adverse effects, indicated by the exceedance of critical limits for specifically chosen endpoint indicators.

The assessment of critical loads using a model-based approach includes the use of geochemical indicators and critical limits or threshold values in a steady-state model. The critical limits can also be used in a dynamic modelling approach to evaluate impacts over time. ‘Risk’ in this book refers to potential impacts caused by exceedances of critical loads (assessed by steady-state models) or critical limit exceedances (assessed by dynamic models). Risk is thus used more loosely than “the probability of occurrence of an (adverse) event, times its (negative) impact (damage)...” as defined by Helbing (2013). Risks refer to potential impacts which occur when exceedances of critical loads or limits are calculated. The use of models helps standardize (risk) assessments at temporal (see Chaps. 8 and 9) as well as regional scale (see Chaps. 21 and 25) for different environmental problems (e.g. Hettelingh et al. 2007).

In the model-based approach, critical loads are derived with steady-state models using critical limits for element concentrations or element ratios in terrestrial and aquatic ecosystems, based on dose-response relationships between these critical limits and the ecosystem status. Using this approach, a critical load of nitrogen, acidity or heavy metals equals the load causing a concentration nitrogen, acidity, aluminium or heavy metals in a compartment (e.g. soil, groundwater, plant, etc.) that does not exceed a critical limit, thus preventing ‘significant harmful effects on specified sensitive elements of the environment’. Consequently, the selection of critical limits is a important step of major importance in deriving a critical load. In computing a critical load one aims at long-term protection of the ecosystem.

This chapter gives an overview of (i) the abiotic impacts of acid, metal and nitrogen deposition on soils and waters with their potential impacts on terrestrial and aquatic ecosystems and (ii) the related geochemical indicators with derived critical limits for acidity (Sect. 2.2), metals (Sect. 2.3) and nitrogen (Sect. 2.4), including a critical evaluation of the usefulness of those limits to assess effects in the field situation. Terrestrial ecosystems are all non-agricultural systems and include both soil and underlying ground water. Aquatic ecosystems include fresh waters, specifi-

cally lakes. The chapter concludes with an overview of derived or applied critical limits (Sect. 2.5).

2.2 Impacts of Acid Deposition on Terrestrial and Aquatic Ecosystems and Critical Limits for Geochemical Indicators

2.2.1 *Terrestrial Ecosystems*

2.2.1.1 Impacts of Acid Deposition

Atmospheric depositions of sulphur (S) and nitrogen compounds have an impact on terrestrial ecosystems through ‘eutrophication by nitrogen’, as discussed in Sect. 2.4, and soil acidification. Some forms of nitrogen (e.g. HNO_3) are directly acidic. In most cases however, N becomes acidifying when reduced forms of N are oxidized to NO_3^- via nitrification. Soil acidification is characterised by a wide variety of long-term effects. It is defined as the loss of Acid Neutralizing Capacity (ANC) and ultimately leads to a decrease in soil pH. Changes in soil pH are dependent on the buffering capacity of the soil (e.g. Ulrich 1981).

The link between acid deposition and changes in soil and soil solution chemistry is well documented. Acidifying compounds (N and S) deposited on calcareous soils (including substrates of young moraine regions) at first will not change soil acidity. In these soils protons (H^+) are exchanged on the soil complex for ions such as bicarbonate (HCO_3^-) and calcium (Ca^{2+}), thereby buffering the soil against acidifying processes. HCO_3^- and Ca^{2+} ions leach from the system, but the pH remains the same until almost all of the calcium carbonate has been depleted. In soils dominated by silicate minerals, buffering is taken over by cation exchange processes of the soil adsorption complexes. In these soils, protons are exchanged for calcium (Ca^{2+}), magnesium (Mg^{2+}) and potassium (K^+) and these cations are leached from the soil together with anions (mostly nitrate or sulphate). Subsequent leaching of Ca^{2+} , Mg^{2+} and K^+ leads to loss of the soil’s buffering capacity by base cations and to nutrient imbalances for plant growth. Because of the restricted capacity of this buffering system, soil pH will decrease. Both soil solution chemistry and soil base cation pools are thus affected by acid deposition, both being interdependent. In many catchments, it has been shown that acid deposition has caused prolonged export of base cations, such as Ca^{2+} and Mg^{2+} , from forest soils, resulting in base cation nutrient depletion (Akselsson et al. 2007; Sverdrup et al. 2006; Watmough et al. 2005).

Buffering by cations and leaching will continue until all base cations are exchanged and continuing acidification will lead to a shift in the buffer range of the soil from base cation buffering to aluminium (Al^{3+}) buffering ($\text{pH} < 4.5$). In mineral soils with a large cation exchange capacity and high base saturation, the base cation buffering may continue for several decades, even at relatively high acid inputs.

At low pH (<4.5), hydrous oxides of several metals start to dissolve. This causes a strong increase in dissolved concentrations of Al^{3+} (De Vries et al. 1989; Ulrich 1981) and other metals, such as manganese (Augustin et al. 2005b). Acid deposition on base-poor soils thus leads to mobilization of potentially toxic Al^{3+} (Mulder et al. 1989). Significant correlations between S deposition and enhanced concentrations of Al^{3+} in soil solutions have been demonstrated in acidic forest soils in Europe (De Vries et al. 2003).

Plant growth and species composition of vegetation can be seriously affected by soil acidification, associated with a decrease in pH and base saturation as well as an increase of the concentration of Al^{3+} in the soil solution. It may lead to dominance of acid-resistant plant species and the decline of characteristic species for the intermediate and higher soil pH range (Falkengren-Grerup 1986; Falkengren-Grerup and Tyler 1993). Furthermore, enhanced dissolution of Al by acid deposition has long been considered a probable threat to forest vitality (Ulrich et al. 1980; Ulrich 1984). Hypothesized mechanisms of Al toxicity include hampered root growth and inhibition of uptake of nutrients (Matzner and Murach 1995; Schulze 1989; Sverdrup et al. 1990; Sverdrup and Warfvinge 1993; Sverdrup et al. 1992; Warfvinge et al. 1993). Furthermore, several authors (e.g. Roelofs et al. 1985) showed that release of Al by soil acidification and imbalances of ammonium to base cations, due to excessive N inputs and reduced nitrification, may cause nutrient deficiencies, which may be aggravated by a loss of mycorrhiza or root damage. This coincided with field observations and foliage analyses, showing that deficiencies of Mg and K caused yellowing of needles of Norway spruce (Zöttl and Mies 1983). In the eighties, several authors (for example Hutchinson et al. 1986; Ulrich and Pankrath 1983) considered soil acidification, especially the increase of the concentration of Al^{3+} in soil solution, responsible for forest decline, since Al^{3+} is very likely to be toxic to plant roots (Cronan and Grigal 1995; Marschner 1990; Mengel 1991; Sverdrup and Warfvinge 1993). Currently, the risk of Al^{3+} for forest health in the field is considered lower (see Sect. 2.2.1.3), but the adverse impact of Al^{3+} on root functioning is an established fact, at least under laboratory conditions.

2.2.1.2 Critical Limits of Geochemical Indicators

Ulrich and co-workers (e.g. Ulrich and Matzner 1983) were among the first who postulated that increased Al concentrations, specifically inorganic Al, and elevated Al/Ca ratios in soil solution are a major cause of forest dieback, by damaging the root system of tree species. Effects of high concentrations of Al on trees were tested with seedlings, either grown in water cultures, pot trials or in a greenhouse, mainly during the 1980s. For overviews, we refer to Rengel (1992) and Kinraide (2003). The sensitivity of a tree to Al varies as a function of solution pH, Al speciation, Ca concentration, overall ionic strength, the form of inorganic N (NH_4 or NO_3), mycorrhiza interactions, soil moisture etc. Consequently, a wide range of Al toxicity thresholds for various tree species has been reported in the literature, varying between less than 1.5 and more than 30 mg l^{-1} (e.g. Cronan et al. 1989; Joslin and Wolfe 1988, 1989; Keltjens and van Loenen 1989; McCormick and Steiner 1978;

Ryan et al. 1986a, b; Smit et al. 1987; Steiner et al. 1980; Thornton et al. 1987). The sensitivity increases from red spruce, with significant biomass reductions starting to occur near 2 mg l^{-1} of inorganic Al, to Douglas fir, spruce and European beech, whereas Scots pine, oak and birch are relatively insensitive to Al (Cronan et al. 1989). Results in a variety of laboratory experiments listed above showed that the Ca/Al ratio was a better indicator for root impacts than inorganic Al (Cronan and Grigal 1995; Sverdrup and Warfvinge 1993; Sverdrup et al. 1992). As with Al, a wide range in toxicity thresholds for the Al/Ca ratio has been reported. Based on greenhouse experiments by Rost-Siebert (1983), a critical molar Al/Ca ratios of 1.0 for spruce and 10 for birch was proposed by Ulrich and Matzner (1983). A correlative field study between soil solution chemistry and forest vitality (Roelofs et al. 1985) yielded a critical molar Al/Ca ratio for black pine of 1.0, identical to that for spruce. Furthermore, laboratory experiments with two-year old black pine trees showed a strong decrease in Ca and Mg uptake at Al/Ca ratios above 1 (Boxman and van Dijk 1988). Based on the data given above, an inorganic Al concentration of 0.2 eq m^{-3} (about 2 mg l^{-1}) and a molar Al/Ca ratio of 1.0 has widely been used as geochemical risk indicators in the computation of critical acid loads (e.g. De Vries 1993).

Sverdrup and Warfvinge (1993) carried out a systematic review of impacts of Al on the growth of tree seedlings and plants in laboratory experiments, based on approximately 200 studies. The response in acid soils, as expressed by root growth, stem growth or plant growth in experiments, has been determined for different species of coniferous and deciduous trees. Studies showed that the plant response can be described better as a function of the base cation and Al concentration in soil solution than just as a function of Al alone or a Ca/Al ratio. The critical limit was expressed as a molar Bc/Al ratio, with Al referring to the total Al concentration and Bc denoting $\text{Ca} + \text{Mg} + \text{K}$. As an example, Fig. 2.1 shows the results of dose-response data collected for Norway spruce and the approach used to estimate a critical limit for Bc/Al based on a 20% effect on biomass growth. Based on their study, the Ca/Al ratio was replaced by the Bc/Al ratio. Critical limits were derived for different tree species. A critical Bc/Al ratio is now the most commonly used critical limit (with biomass growth as endpoint) in the calculation of critical loads for forests (De Vries et al. 2003). In many calculations of critical loads of acid deposition to forest ecosystems, either a general limit value of 1 is used for Bc/Al, or a tree species specific value, ranging mostly between 0.5 and 2.0.

Critical acid loads have also been calculated with a critical limit that avoids depletion of secondary Al compounds (e.g. De Vries 1993; De Vries et al. 1994). This so-called Al depletion criterion is based on the idea that the acceptable rate of Al leaching should not be larger than the rate of Al mobilization by weathering of primary minerals. Otherwise, the remaining part of Al has to be supplied from secondary Al compounds. This causes depletion of these compounds, which might induce an increase in Fe buffering, which in turn leads to a decrease in the availability of phosphate (De Vries and Kros 1989). Negligible depletion of secondary Al compounds is achieved when Al leaching equals mobilization of Al from primary minerals. The critical inorganic Al concentration is thus calculated as:

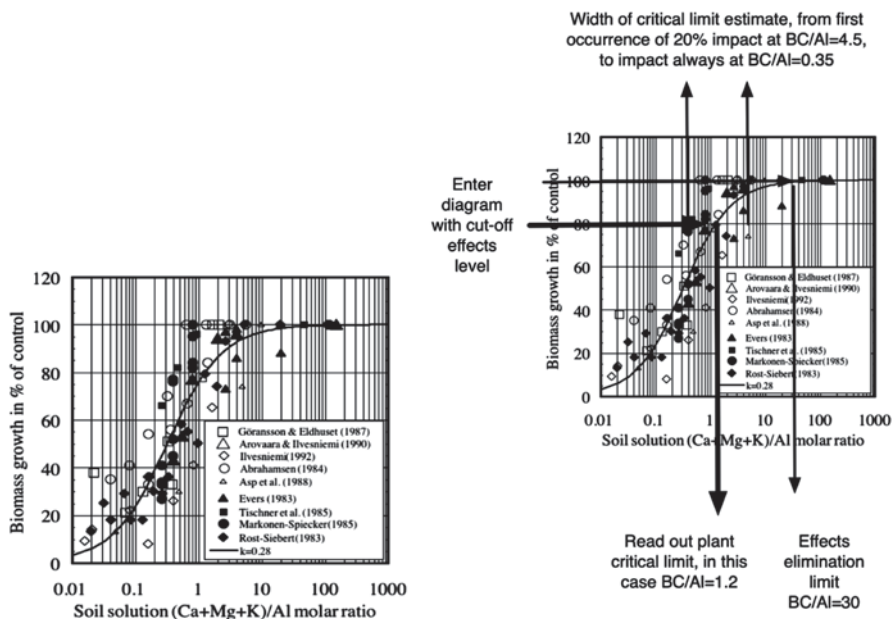


Fig. 2.1 Dose-response data collected for Norway spruce (*left*) and the approach that was used to estimate a critical limit for Bc/Al_{tot} based on a 20% effect on biomass growth (*right*). Using a fitted response, this yielded a critical limit for $Bc/Al_{tot} = 1.2$, with 20% effect in all experiments at $Bc/Al_{tot} = 0.35$, while the first incidence of 20% impact begins at $Bc/Al_{tot} = 4.5$ (After Sverdrup and Warfvinge 1993)

$$[Al_i]_{crit} = r \cdot BC_{we} / Q \quad (2.1)$$

where $[Al_i]_{crit}$ is the critical inorganic Al concentration (eq m^{-3}), BC_{we} is base cation weathering ($\text{eq ha}^{-1}\text{yr}^{-1}$), r is the equivalent stoichiometric ratio of Al to BC in the congruent weathering of silicates (primary minerals) and Q is the precipitation excess ($\text{m}^3 \text{ha}^{-1}\text{yr}^{-1}$).

An aspect to be mentioned regarding Al is the fact that the free Al^{3+} is considered to be toxic, and not the organically complexed Al species. Unlike metals (see Sect. 2.3), critical limits have only been derived for total Al^{3+} concentration, but not for the free Al^{3+} . In Fig. 2.2 $[Al^{3+}]$, $[Al(OH)^{2+}] + [Al(OH)_2^+] + [Al(OH)_3^0] + [Al(OH)_4^-]$ and $[\Sigma Al_{org}]$ are shown as shares (in moles) of $[Al_{tot}]$ for a range of pH-values, computed for triprotic organic acids. For high values of DOC it shows that free Al dominates below $\text{pH}=2.5$, organic Al dominates between pH 4 and 6, whereas Al-hydroxides dominate above $\text{pH}=7$. The graph illustrates that the share of Al^{3+} is highly dependent on pH and DOC. The problem with re-analysis of laboratory data is that DOC values are generally not available, thus leaving Bc/Al_{tot} as the current risk indicator for acidification.

Apart from ecosystem impacts, Al may also cause health effects, especially by intake in drinking water. No health-based guideline value for aluminium was however recommended in the WHO Guidelines for drinking water quality (WHO

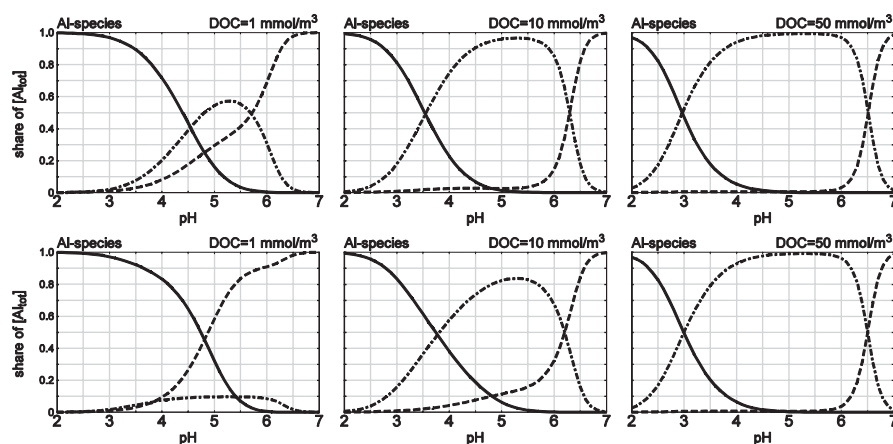


Fig. 2.2 $[Al^{3+}]$ (solid line), $[AlOH^{2+}] + [Al(OH)_2^+] + [Al(OH)_3^0] + [Al(OH)_4^-]$ (dashed line) and $[\Sigma Al_{org}]$ (dashed-dotted line) as shares of $[Al_{tot}]$ as a function of pH for $m \cdot DOC = 1$ (left), 10 (centre) and 50 $mmol\ m^{-3}$ (right) for $[Al_{tot}] = 1$ (top row) and $[Al_{tot}] = 10\ \mu mol\ l^{-1}$ (bottom row). No complexation with other ions is considered

2004). It was concluded that epidemiological and physiological evidence did not support a causal role for aluminium in Alzheimer disease. An aluminium concentration of $0.2\ mg\ l^{-1}$ in drinking-water is, however, provided a compromise between the practical use of aluminium salts in water treatment and discoloration of distributed water. This is used as an indicator parameter in the EU Drinking Water Directive (EC 1998).

2.2.1.3 Evaluation of Critical Limits of Geochemical Indicators in View of Field Effects

The relevance of laboratory experiments addressing Al toxicity under field conditions has been disputed (Binkley and Högborg 1997; De Wit et al. 2001b; Kreutzer 1995; Løkke et al. 1996). Indeed, healthy trees have been found at sites where high soil solution Al concentrations were measured (Huber et al. 2004), while nutrient deficiency symptoms in trees have been found at other sites with similar conditions (Alewell et al. 2000). In addition, whole-ecosystem experiments, designed to test effects of acid deposition on forests (Abrahamsen et al. 1993a; Beier et al. 1998; Huber et al. 2004; Kreutzer and Weiss 1998), have been inconclusive with respect to Al-toxicity effects on root growth and nutrient uptake. For example, field manipulations in forest ecosystems conducted to study effects of N and acid deposition on forest ecosystems, such as in Skogaby in Sweden (Nilsson and Wiklund 1995a, b), Nordmoen in Norway (Abrahamsen et al. 1993b), Höglwald in Germany (Huber et al. 2004; Kreutzer and Weiss 1998; Kreutzer et al. 1998; Nowotny et al. 1998; Rothe et al. 2002) and various experiments across Europe in the so-called NITREX

and EXMAN sites (Beier et al. 1998; Boxman et al. 1995) are all difficult to interpret with respect to the specific effect of Al on forest health. Manipulations in the NITREX and the Skogaby experiments included the addition of N fertilizer to forest plots, potentially affecting both tree (Matson et al. 2002) and root growth (Persson and Majdi 1995), and are thus not suitable to specifically test the effects of Al toxicity. In EXMAN, roofs were constructed to avoid acid deposition from reaching the forest soil and enable clean water irrigation. The response of the forest was studied with the aim to understand recovery of forest under reduced acid deposition. Roof experiments also reduced N inputs compared to an open-sky situation. After 10 years of 'clean rain' in Solling (Germany) fine root growth increased, which was interpreted as an compensatory effect to reduced N inputs and not of reduced acidification (Lamersdorf and Borken 2004). In a previous acid manipulation experiment close to Nordmoen (Abrahamsen et al. 1993b), acid manipulation reduced the foliar content of Ca and Mg. This effect was, however, attributed to depleted soil pools of Ca and Mg. Impacts of Al toxicity could not be assessed, as soil solution chemistry was not investigated. In short, reasons for the inconclusiveness of field experiments include a lack of data collection describing below-ground processes and the addition or removal of N, which in itself may affect root and tree growth.

An important forest manipulation study explicitly designed to test the Al-toxicity hypothesis was a 7-year (1997–2003) experiment in a middle-aged Norway spruce stand at Nordmoen, Norway (De Wit et al. 2001a, b, 2010). The objective of the study was to quantify effects of chronically enhanced soil solution concentrations of inorganic Al on fine roots, on nutrient concentrations in needles, bark and fine roots, on tree growth and on crown condition. The site had low concentrations of Al and N in the control treatment. After three years of treatment, no effect was found on tree volume, annual increment, height increment, crown density or crown condition (De Wit et al. 2001b). Investigations of fine root growth using root ingrowth cores in the manipulated plots at Nordmoen also did not show any treatment responses in fine root biomass or necromass (Eldhuset et al. 2006; Nygaard and de Wit 2004). No other vegetation responses than changes in tree nutrient status were found. The most significant and consistent response to the experimental manipulation was the decline in Mg content of needles in the most extreme treatment, caused by reduced Mg uptake by the roots in response to Al addition. Strong competitive inhibition of Al^{3+} ions on Ca^{2+} and Mg^{2+} ion adsorption has been demonstrated in roots of *P. abies* (Schröder et al. 1988) and *P. rubens* (Cronan 1991). The presence of ectomycorrhiza associated with tree roots in the field, lacking in nutrient solution experiments, may have a protective effect against Al (Ahonen-Jonnarth et al. 2003). In summary, the field manipulation experiment at Nordmoen showed that the increased soil solution Al concentrations did not affect fine root growth and mortality, contrary to the hypothesized effects of toxic Al on fine roots, but reduced Mg uptake in extreme situations. One may criticize that 3 years (root impacts) to 7 years (foliar chemistry) of data is insufficient to test the hypothesis of reduced base cation uptake due to impacts of Al toxicity on root growth, because of a large base cation store in the soil, but it is at least an indication that results of (generally much shorter) laboratory experiments may deviate from those in field situations.

An often heard criticism of, mostly relatively short-term, field manipulation studies is the fact that the existence of a time delay between deposition changes and ecosystem effects may obscure results. This does not hold for studies comparing data on exposures and responses in long-term or large-scale field surveys. However, analyses of large data sets, obtained from European forest ecosystems monitoring programs, are unable to confirm the hypothesized relations between forest vitality and Al toxicity unambiguously due to confounding factors. Augustaitis and Bytnerowicz (2008) found that acidifying air compounds and their deposition are key factors explaining changes in Scots pine defoliation and stem growth in Lithuania. By applying a linear multiple regression technique, they found that 23–28% of the variance of residual defoliation and 18.5% of variability in stem increment residuals of pine trees was explained by acid deposition. However, the link to Al in soil solution is not clear from those analyses. Furthermore, on a European scale, clear relations have been demonstrated between acid deposition and soil acidification (De Vries et al. 2003) but not between forest health (crown condition) and acid deposition (Fischer et al. 2007; Klap et al. 2000). Rather, they point at additional confounding factors, such as site conditions, stand age, insect and fungi attacks, and weather conditions, which make it difficult to attribute observed patterns in crown condition to Al only. There is also a lack of clear relations between forest vitality and exceedances of critical loads (Løkke et al. 1996; Watmough and Dillon 2003). Akselsson et al. (2004) found no significant relation between forest damage in the most exposed part of the Czech Republic and the exceedance of critical loads, using the Bc/Al ratio as indicator. Nellemann and Frogner (1994) found a relationship between defoliation and modelled exceedance of critical loads based on about 100 forested plots throughout Europe, but Solberg et al. (2002), who used a stratum of about 100 old forest officers' plots, found no such relationship. Their soil solution Al/Ca data were, however, mostly below the critical limit of 1.0, demonstrating that modelled exceedance does not mean that unfavourable soil solution chemistry is present today, when critical loads are exceeded, but only that it might be reached sometime in the future. Hence, critical load exceedance may not be an appropriate variable in correlative studies searching for acid deposition effects.

Although current field data cannot show an unequivocal relationship between soil solution chemistry and forest vitality or forest growth, they do indicate that both Al concentrations and base cation stores should be considered in a risk evaluation of acid deposition. For example, long-term records from an acidified nutrient-poor spruce forest stand in Germany showed strong signs of nutrient deficiency with small pools of exchangeable Ca and Mg (Alewell et al. 2000). Furthermore, Lawrence et al. (2005) compared changes in soil chemistry, based on archived soil samples in 1926, 1964, and 2001, with patterns of tree growth in the same period near St. Petersburg, Russia. Results showed a depletion of exchangeable Ca and Mg in the period between 1926 and 1964 and an increase in exchangeable Al between 1964 and 2001. In accordance with soil buffering theories (De Vries et al. 1989; Ulrich 1981), inputs of acidity were first (1926–1964) neutralized by replacement of exchangeable Ca and Mg by H, while continued acid deposition (1964–2001) mobilized readily available Al, with related exchange of Ca, Mg and H by Al. The

onset of Al mobilization coincided with decreased diameter growth and a suppression of climate-tree growth relationships in Norway spruce. This suggests that the trees were responding to both a decline in Ca and Mg availability and an increase in Al mobilization.

In summary, forest vitality variables, such as tree growth, fine root growth and defoliation, do not show a clear response to raised soil solution Al concentrations and decreased Bc/Al ratios in both field manipulation experiments and monitoring studies within the time horizon of these experiments and studies. This suggests that forests may be more resilient to (magnitude and duration of) acidification stress than previously thought. This is because the Bc/Al ratio, representing the acidification component of disturbance, is only one of many endpoint indicators affecting other damage parameters, such as water availability, N deposition, climate change including extreme events, ozone exposure, etc. (Sverdrup et al. 2007). Following the definition of critical loads, one should, however, keep in mind that critical limits represent minimum no-effect levels. Augustin et al. (2005a) thus argue that the critical limits for forest soil acidification aim to identify a starting point of an 'unfavourable acid stress' situation, that can ultimately lead to damage. The risk for damage includes, e.g., reducing the resilience of forests to extreme environmental conditions such as storms (Braun et al. 2003).

The limitation of the use of Bc/Al ratios and dissolved Al concentrations in critical load assessments has already been mentioned early in the nineties due to the lack of good correlations between those parameters and forest health. For example, in calculating critical load exceedances for European forests, De Vries et al. (1994) conclude their article with "For a correct interpretation of critical loads, it should be emphasized that an exceedance does not necessarily cause a visible effect on forests, due to the complex interactions in these ecosystems. They mainly have a signal function. However, an exceedance of the critical loads involves a certain risk to the health of forests which increases with the magnitude and the duration of the exceedance". It is in the light of this signal function that these parameters can be used.

2.2.2 *Aquatic Ecosystems*

2.2.2.1 **Impacts of Acid Deposition**

In acidic soils, acid deposition causes Al release from soils in the watershed that leaches into lakes and streams. There are well documented, large-scale effects of acid deposition on aquatic ecosystems. The earliest reports linking dead fish and declining fish populations to acid rain and surface water acidification appeared in the early 1970s in both Scandinavia and North-America (Beamish and Harvey 1972; Beamish 1974; Hultberg and Stenson 1970; Jensen and Snekvik 1972; Leivestad and Muniz 1976). Evidence for large scale die-back of fish populations in the Nordic countries became evident in the 1980s. For example, in Norway an estimated 8000 lakes lost their fish population (Hesthagen et al. 1999). Severe impacts,

on fish as well as other organisms were also reported for Sweden, Finland, the UK, Canada and the USA (Gray et al. 2012; Monteith et al. 2005; Tammi et al. 2003).

The mechanisms inducing the fish kills and other biological effects are linked to low pH in combination with high Al concentrations. Both low pH (Schofield 1976) and increased Al levels (Baker and Schofield 1982) are directly toxic to fish. Effects include mortality of adult fish and recruitment failure, visible as different patterns in age classes of the fish population (Hesthagen et al. 2011). In addition, low pH and increased Al levels cause chronic stress that may not kill individual fish, but lead to a lower body weight and smaller size, either as a chronic effect on the fish or as indirect effects of changes in food and habitat (Lien et al. 1996). Some types of plants and animals are able to tolerate acidic waters. Others, however, are acid-sensitive and will be lost as the pH declines.

Time trend data have recently become available, not only showing clear evidence of chemical recovery from surface water acidification, but also biological recovery. One well-documented long-term dataset is from Lake Saudlandsvatn in southernmost Norway, where time trend data of brown trout (*Salmo trutta*), caddisfly (*Hydropsyche siltalai*) and zooplankton (*Daphnia longispina*) is available together with water chemistry data. The lake was highly acidified, with episodic pH below 5.0 in the 1970s and 1980s, and the critical load exceeded fivefold (Hesthagen et al. 2011). Chemical recovery following reduced S deposition is observed since the late 1990s and the S deposition dropped below the critical load around 2000. The brown trout population was stable until the early 1980s, then started to decline and nearly went extinct in the 1990s and started to recover ever since. Parallel with the trends in water chemistry it was also observed that the caddisfly disappeared from the tributaries in the 1980s, but reappeared in 1996 and increased in abundance from 2000 onwards. Recovery in all three organism groups coincided with an ANC of $>20 \text{ meq m}^{-3}$ and toxic inorganic Al concentration of $<30 \text{ mg m}^{-3}$ (Hesthagen et al. 2011).

2.2.2.2 Critical Limits of Geochemical Indicators

Critical limits for surface waters are generally derived for the protection of aquatic organisms, mostly fish species, but also invertebrates and aquatic plant species are used as indicators. The link between water chemistry and freshwater fauna has mostly been evaluated from survey data, used to establish empirical relationships between water chemistry parameters and presence-absence data of organisms. In general, low pH and high inorganic Al concentrations correlate with damaged and/or extinct organisms. In one of the earlier studies Schofield (1976) looked at the correlation between fish status and water pH, whereas Baker and Schofield (1982) report on the effects of inorganic Al on several fish species in their growth stages.

Jeffries and Lam (1993) used a critical pH=6 to determine critical loads (of wet sulphate deposition) for Canadian lakes with the aim of protecting fish and other aquatic organisms. Rask et al. (1995) derived critical values of pH and labile Al, using Finnish lake survey data. Critical annual average pH values, at which

fish populations were affected, were 5.0 for perch and 5.8 for roach, while values at which these fish were lost were 4.8 and 5.5, respectively. Comparable values were derived by Hultberg (1988). Critical annual average concentrations of labile Al, at which fish populations were affected, varied from 90 mg m⁻³ for perch and 20 mg m⁻³ for roach. Hultberg (1988) gave a value of 50 mg m⁻³ for perch, but one has to keep in mind that water properties other than pH and labile Al also affect the toxicity of acidic water.

But it is mostly ANC that has been used to define critical chemical limits for surface waters. Of course, pH, [Al] and ANC are interrelated, as discussed in more detail in Chap. 6, but not one-to-one; their relationship depends, in addition to the partial pressure of CO₂, mostly on the amount of dissociated organic anions and complexed Al. The advantage of ANC is that it is a robust variable, e.g., it is not affected by the partial pressure of CO₂.

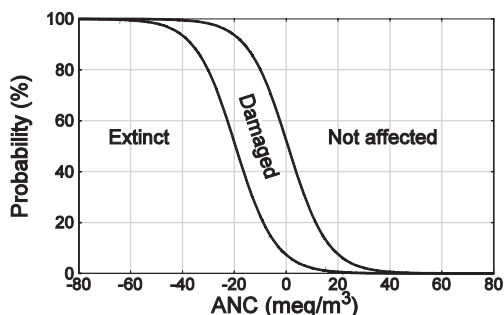
Lien et al. (1996) analysed the status of fish and invertebrate populations in the context of surface water acidification and loss of ANC in 1095 Norwegian lakes. The data for fish population status came from interview surveys among fishery managers, while lake chemistry data for the same lakes were mostly based on a 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 the acidification of lakes. Based on an evaluation of fish and invertebrate populations, a lower limit of $[ANC] = 20 \text{ meq m}^{-3}$ was suggested as the critical limit for Norwegian surface waters (Lien et al. 1996, see Fig. 2.3). This limit has been widely used (southern central Alps: Boggero et al. 1998; China: Duan et al. 2000; Kola, northern Russia: Moiseenko 1994; Nordic countries: Posch et al. 1997). Other values used were zero in the United Kingdom (CLAG 1995) and 40 meq m⁻³ in south-central Ontario, Canada (Henriksen et al. 2002).

Figure 2.3 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. This could mean 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. With this in mind, Henriksen et al. (1995) derived an ANC-limit that depends on catchment characteristics, such as deposition and runoff.

Lydersen et al. (2004) argued that the ANC-limit should be corrected for the amount of organic acids present in the lake. They revisited the database for water chemistry and fish status and showed that the fit between observed fish status and ANC can be (slightly) improved, if an ‘organic acid adjusted’ ANC, $[ANC]_{\text{oa}}$, is used. This quantity they defined as:

$$[ANC]_{\text{oa}} = [ANC] - \frac{1}{3} \cdot m \cdot \text{TOC} \quad (2.2)$$

Fig. 2.3 Relationship between the ANC concentration in lake water and the probability for damage and extinction of fish (brown trout) populations in lakes, derived from Norwegian data (after Lien et al. 1996)



where $m \cdot TOC$ is the total organic carbon expressed in meq m^{-3} with m being the charge density, with $m = 10.2 \text{ meq gC}^{-1}$ chosen by Lydersen et al. (2004), and the factor $1/3$ arising from the assumption that one third of organic acids should be counted as strong acids. Using a 95% probability of no damage to fish populations—as was done for deriving the classical ANC-limit of 20 meq m^{-3} by Lien et al. (1996)—they obtained an $[ANC]_{\text{aaa}}$ limit of 8 meq m^{-3} for brown trout (*Salmo trutta*), -2 meq m^{-3} for perch (*Perca fluviatilis*) and 11 meq m^{-3} for arctic char (*Salvelinus alpinus*). From these the ANC-limit to be used in critical load calculations is obtained as:

$$[ANC]_{\text{lim}} = [ANC]_{\text{aaa,lim}} + \frac{1}{3} \cdot m \cdot TOC \quad (2.3)$$

i.e. the ANC-limit becomes dependent on the surface water considered. These lake- and fish-specific ANC-limits have been used in studies deriving critical loads for surface waters in Norway (Larssen et al. 2008) and Finland (Posch et al. 2012).

2.3 Impacts of Metal Deposition on Terrestrial and Aquatic Ecosystems and Critical Limits of Geochemical Indicators

2.3.1 Terrestrial Ecosystems

2.3.1.1 Impacts of Metal Inputs

Metals are naturally occurring constituents in the environment. Several metals, such as copper (Cu) and zinc (Zn) are essential for living organisms, because of their role in various physiological and biochemical processes. For other metals, such as cadmium (Cd), lead (Pb) and mercury (Hg), no biological functions are known (Clark 2001). A description of major pathways of metals in terrestrial ecosystems, including the link with aquatic ecosystems, is given in Fig. 2.4.

With respect to risks of heavy metal deposition for terrestrial ecosystems, a distinction can be made between effects on the health of (i) soil organisms/processes

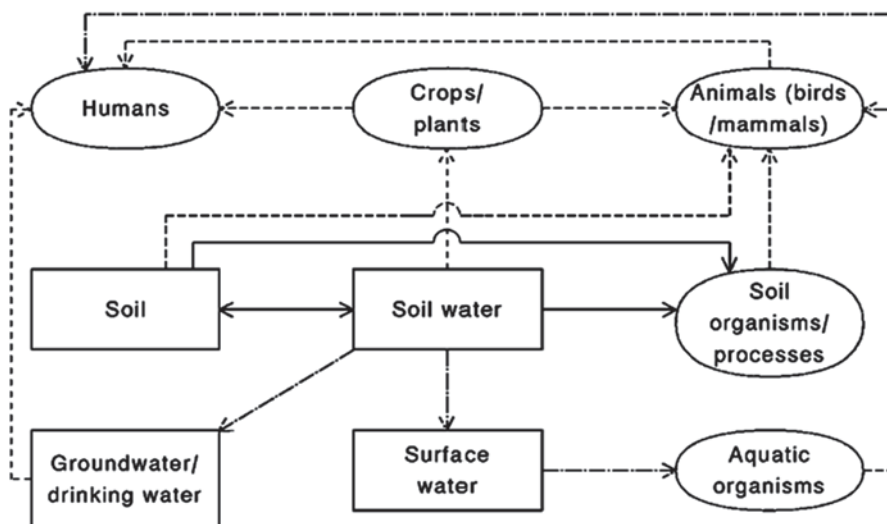


Fig. 2.4 Overview of the fluxes and impact pathways of metals from the soil to other compartments in terrestrial and aquatic ecosystems. Boxes are key 'pools' and ovals are key 'receptors'. (De Vries et al. 2007b)

and plants (Bringmark et al. 1998; Palmborg et al. 1998) (primary ecotoxicological risks), and (ii) animals, including both domestic and wild animals, and humans that use ground water as drinking water or that consume crops, meat or fish (Clark 2001) (secondary poisoning).

Effects on soil organisms, including micro-organisms/macro-fungi and soil fauna, such as nematodes and earthworms, include reduced species diversity, abundance and biomass, and changes in microbe-mediated processes (Bengtsson and Tranvik 1989; Giller et al. 1998; Vig et al. 2003). Effects on vascular plants include reduced development and growth of roots and shoots (toxicity symptoms), elevated concentrations of starch and total sugar, decreased nutrient contents in foliar tissues (physiological symptoms) and decreased enzymatic activity (biochemical symptoms) (Das et al. 1997; Prasad 1995). A review of these phytotoxic effects is given by Balsberg-Påhlsson (1989).

Effects on microorganisms, plants and, to a large extent, also on invertebrates occur through the soil solution (Ritchie and Sposito 2001). In accordance with the principles of the free ion activity model (FIAM) (Campbell 1995; Morel 1983) and the Biotic Ligand Model (BLM) (Di Toro et al. 2001; Thakali et al. 2006), metal uptake leading to toxicity can be considered to occur through interaction of the free metal ion (FMI) in soil solution (e.g. Cd^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+}) with the organism. The extent of this interaction, and thus the degree of toxic effect due to a given FMI concentration, also depends on the concentrations of solution cations (e.g. H^+ , Na^+ , Ca^{2+}) that in the BLM framework compete with the toxic metal for binding to the organism.

Next to effects on soil organisms, metals may be transferred via food chains affecting (i) humans through reduced food quality of crops and animal products

and (ii) animal health through accumulation of metals in organs of cattle, birds and mammals. Heavy metal accumulation in food chains is important with respect to Cd and Hg, and to a lesser extent for Pb. In agriculture, it is specifically high Cd inputs that may lead to agricultural products violating food quality criteria (Alloway 1990; Fergusson 1990).

2.3.1.2 Critical Limits of Geochemical Indicators

Relevant receptors in terrestrial ecosystems are arable land, grassland and non-agricultural land (forests, heathlands, grasslands and peatlands). Possible effects on soil organisms and plants (phytotoxicity) and terrestrial fauna are of concern in all types of ecosystems. Furthermore, impacts on food quality are relevant for arable land and grassland (limits for animal food), whereas possible secondary poisoning effects on animals are relevant in grassland (cattle) and non-agricultural land (wild animals). Critical limits define the threshold of potential risk to a defined receptor, and have been defined in relation to ecotoxicological or human-toxicological risks, such as:

- Soil: critical limits related to effects on soil organisms (micro-organisms and soil invertebrates) and plants (mg kg^{-1}).
- Plants/terrestrial fauna: critical limits in plant tissue, animal products (meat) or target organs, such as kidney, related to effects on plants and/or animals and on humans by consumption (food quality criteria) (mg kg^{-1}).
- Ground water: critical limits in drinking water related to effects on humans by consumption (mg m^{-3} or $\mu\text{g l}^{-1}$).

Food quality criteria for metals in food crops and animal products, in view of human-toxicological risks, are relevant in agriculture. Critical limits for terrestrial ecosystems (often also denoted as Predicted No Effect Concentrations or PNECs) are limited to ecotoxicological effects on soil organisms and plants, while impacts on aquatic systems are related ecotoxicological effects on aquatic organisms. These limits are in principle derived from No Observed Effect Concentrations (NOECs) for metal contents in either soil, based on laboratory studies with plants and soil organisms, such as soil micro-biota and soil invertebrates (Tyler 1992) or surface water, based on laboratory studies with aquatic organisms.

In soils, the risks from heavy metals, however, depend on their availability, which is influenced by soil properties such as pH, clay and organic matter content (Boekhold et al. 1993; Groenenberg et al. 2010; Sauvé et al. 2000). The use of a single soil metal concentration as a critical limit for ecotoxicological effects upon soil organisms has therefore been criticized (Allen 1993) since it does not account for observed variations in the toxicity of cationic metals among soils of differing chemistry (Spurgeon and Hopkin 1996). The impacts of soil properties on the bioavailability and toxicity of metals thus has to be accounted for in critical limit derivations. Free metals in soil solution are the major pathway for metal impacts on plants, micro-organisms and soft-bodied invertebrates, such as earthworms (Saxe et al. 2001). Thus, an approach to set critical limits for the FMI is particularly

appropriate to evaluate the risks of effects. In view of critical load assessments for terrestrial ecosystems, there is also a need for critical metal concentrations in soil solution since the critical metal leaching rate is the most important term in deriving critical loads.

Since total metal or free ion concentrations in soil solution are hardly ever measured, such concentrations need to be derived using models for solid-solution partitioning and speciation of metals in soil solution. In this context, empirical models (so-called transfer functions) for solid-solution partitioning can be used, which relate metal concentrations in solution to metal concentrations in the solid phase, accounting for the impact of soil properties.

2.3.1.3 Approach to Derive Critical Limits for Total Dissolved Metal Concentrations

Critical Dissolved Metal Concentrations Related to Impacts on Soil and Aquatic Organisms: The approach to derive critical limits for Cd, Pb, Hg, Cu and Zn for soil and surface water is based on the standard approach developed by the Organisation for Economic Co-operation and Development (OECD) calculating Maximum Permissible Concentrations (MPCs) of substances (OECD 1989). MPCs are calculated by extrapolation of No Observed Effects Concentrations (NOEC levels) or Lowest Observed Effects Concentration (LOECs) for metals in soils or surface water, based on chronic toxicity tests for single species, mostly assuming a log-logistic, or log-normal distribution of species sensitivities (Slooff 1992). From a range of NOEC data, the hazardous concentration at which $p\%$ of the species in an ecosystem are potentially affected (HC_p), implying that $100-p\%$ are protected, can be derived from the ‘species sensitivities distribution’ (SSD). A critical limit for a certain compound is set at HC_5 , meaning that theoretically 95 % of the species within an ecosystem are protected. Using this method, the 95 % protection level calculated with 50 % confidence is regarded as the maximum permissible concentration ($MPC = HC_5$).

Critical Reactive and Total Metal Concentrations in the Soil Solid Phase: Critical reactive soil concentrations for Cd, Pb, Cu and Zn have been derived by Lofts et al. (2004) and De Vries et al. (2007b) on the basis of NOECs for the concentration of added (reactive) metal in laboratory experiments. The data set included (i) decomposers, comprising micro-organisms or microbe-mediated soil processes (e.g. enzymatic activity), (ii) consumers, such as invertebrates (earthworms and arthropods) and (iii) primary producers, specifically plants, drawn from several draft reports on EU Risk Assessment procedures for these metals. The impact of soil properties affecting the bioavailability and toxicity of metals has been accounted for by relating the critical value to soil solution pH and soil organic matter content, according to (log stands for \log_{10}):

$$\log ctM_{re,crit} = b_0 + b_1 \cdot pH + b_2 \cdot \log OM \quad (2.4)$$

where $ctM_{re,crit}$ is the critical reactive metal concentration in the soil (mg kg^{-1}); pH is the soil solution pH and OM is the soil organic matter content (%). Values derived for b_0 , b_1 and b_2 are given in De Vries et al. (2007b). Critical total metal concentrations can be derived by a relationship with concentrations of reactive metal and soil properties, including pH, soil organic matter content and clay, according to (Römken et al. 2004):

$$\log ctM_{tot,crit} = c_0 + c_1 \cdot \log ctM_{re,crit} + c_2 \cdot \log OM + c_3 \cdot \log clay \quad (2.5)$$

where $ctM_{tot,crit}$ is the critical total metal concentration in the soil (mg kg^{-1}) and $clay$ is the clay content (%). Values for c_0 – c_3 are given in De Vries et al. (2007b).

Critical Limits for Free Metal Ion and Total Metal Concentrations in Soil Solution: Lofts et al. (2004) and De Vries et al. (2007b) modified the standard OECD approach for calculating MPCs to assess critical limits for metals in soil solution as a function of soil properties. Since NOEC data on free ionic Cd, Pb, Cu and Zn concentrations in soil solution are hardly available, critical limit functions for metals in soil and soil solution were derived from NOEC and EC_{10} (Effect Concentrations affecting 10 % of the organisms) toxicity data on (i) organisms which are exposed to the metal via the soil solution (plants, micro-organisms and soft bodied soil invertebrates), (ii) accompanied by data on soil properties (pH and organic matter content) to allow the calculation of dissolved concentrations by using Freundlich adsorption constants that depend on those properties (called transfer functions) and (iii) evaluated by a statistical approach deriving limits based on a 95 % protection level. The critical FMI concentrations were derived as a function of soil solution pH, according to (De Vries et al. 2007b, Lofts et al. 2004):

$$\log[M]_{free,crit} = \alpha_{crit} \cdot pH + \gamma_{crit} \quad (2.6)$$

where $[M]_{free,crit}$ is the critical FMI concentration (mol l^{-1}). The pH dependence of the critical FMI concentration is considered to result from a ‘protective’ effect of H^+ against toxicity, resulting from the competitive interactions of solution cations with the organism, as noted before. More recently, the same approach was applied for Ni and Hg (Tipping et al. 2010). Values used for the empirical coefficients α_{crit} and γ_{crit} for Cd, Cu, Pb, Zn, Ni and Hg are given in Table 2.1. More information on the approach and the data sets used is given in Lofts et al. (2004) and De Vries et al. (2007b) for Cd, Cu, Pb, Zn, in Ashmore et al. (2007) for Ni and in Tipping et al. (2010) for Hg. Results are based on the same data sets as those for which the critical reactive metal concentrations were derived. The critical limits for Hg are substantially lower than those of other divalent cationic metals (Table 2.1).

When the critical limit is defined in terms of a critical FMI concentration, the total metal concentration in soil solution, $[M]_{tot}$ (mol m^{-3}), has to be determined as the sum of the concentration of (i) the FMI, $[M]_{free}$ (mol m^{-3}), (ii) dissolved inorganic complexes, $[M]_{DIC}$ (mol m^{-3}) such as MOH^+ , $MHCO_3^+$, MCl^+ , and (iii) metals bound to dissolved organic matter, $[M]_{DOM}$ (mol kg^{-1} DOM), according to:

Table 2.1 Values for α_{crit} and γ_{crit} used to calculate critical limits for free metal ion ($[M]_{free}$) concentrations in soil solution

Metal ^a	α_{crit}			γ_{crit}		
	Lofts et al. (2004)	De Vries et al. (2007b)	Ashmore et al. (2007) ^b	Lofts et al. (2004)	De Vries et al. (2007b)	Ashmore et al. (2007) ^b
Cd	−0.43	−0.32	−0.31	−5.66	−6.34	−6.36
Pb	−0.83	−0.91	−0.93	−4.80	−3.80	−3.50
Cu	−1.21	−1.23	−1.26	−2.57	−2.05	−1.80
Zn	−0.34	−0.31	−0.25	−4.66	−4.63	−5.07
Ni	–	–	−0.42	–	–	−3.78
Hg	–	–	−2.15	–	–	−17.10

^a Datasets used for the derivation include micro-organisms, invertebrates (earthworms and arthropods) and plants. The number of data points is 63 for Cd, 49 for Pb, 141 for Cu, 92 for Zn, 83 for Ni and 52 for Hg

^b Data for Hg are based on results presented in Tipping et al. (2010), whereas the other results are taken from Ashmore et al. (2007)

$$[M]_{tot} = [M]_{free} + [M]_{DIC} + [M]_{DOM} \cdot [DOM] \quad (2.7)$$

where $[DOM]$ is the concentration of dissolved organic matter (kg m^{-3}). By assuming geochemical equilibrium, the partitioning and speciation of metals over the various fractions can be calculated, as described in more detail in Chap. 7.

Critical Dissolved Metal Concentrations Related to Impacts on Human and Animal Health: Human and animal health effects due to metal intake are caused by the uptake of heavy metals via drinking water and crops and in case of humans also livestock products and fish. To protect ground water that is used for drinking water, WHO (2004) uses limits for Cd, Pb and Hg concentrations of 3, 10 and $1 \mu\text{g l}^{-1}$, respectively. These critical limits can directly be used in critical load calculations by applying them as limits for total concentrations in soil drainage water. Critical metal concentrations in plants or animal organs, in view of food quality or crop/animal health, can be combined with relationships for soil-plant transfer, soil-animal transfer and plant-animal transfer to assess related critical total metal concentrations in soil (e.g. De Vries et al. 2007b). Critical limits for the total metal concentration in soil solution can then be derived from a relationship with the total soil metal concentration, as discussed below.

Food quality criteria for metals in crops or target organs (liver and kidney) of grazing animals are available for Cd, Pb and Hg only (see e.g. De Vries et al. 2007b). The EU regulation (EG) No.466/2001 (EU 2001) used fresh weight critical limits for wheat of 0.10 mg kg^{-1} for Cd, 0.20 mg kg^{-1} for Pb and 0.03 mg kg^{-1} for Hg. Critical limits for vegetables were 0.20 mg kg^{-1} for Cd, 0.30 mg kg^{-1} for Pb and 0.03 mg kg^{-1} for Hg. The critical limit for Cd in wheat grains was later amended

Table 2.2 Values for the coefficients a_0 – a_3 and m in the soil-plant relation (Eq. 2.8) for Cd in grass, maize, sugar beet, wheat and lettuce (after De Vries et al. 2008)

Crop	a_0	a_1	a_2	a_3	m	R^2	se- y_{est} ^a
Grass	1.45	–0.38	–	–	1.22	0.63	0.23
Maize	0.90	–0.21	–	–0.32	1.08	0.50	0.28
Sugar beet	1.33	–0.22	–	–0.13	0.62	0.83	0.15
Wheat	0.22	–0.12	–0.33	–0.04	0.62	0.64	0.20
Lettuce	2.55	–0.33	–0.39	–0.19	0.85	0.71	0.08

^a Standard error of the y-estimate on a logarithmic basis

by (EC) No 629/2008 to 0.20 mg kg^{–1} fresh weight. This limit is, however, not based on effects but on the ALARA principle, i.e. “As Low As Reasonably Achievable”. An effects-based critical limit for Cd in cereals (wheat) of 0.10 mg kg^{–1} (fresh weight) was recommended for use under the Long-range Transboundary Air Pollution (LRTAP) Convention (Schütze et al. 2003). Critical contents of Cd, Pb and Hg in meat of cows and sheep in view of food safety equal 0.05, 0.10 and 0.05 mg kg^{–1} (fresh weight), respectively (EU 2001). Data for the toxic impacts on animals can be derived for all metals based on an acceptable daily intake (ADI).

Critical total soil metal concentrations can be derived from critical metal contents in plants from a non-linear relationship between both metal concentrations, accounting for the impact of soil properties that control the (bio)availability of metals in soils (Adams et al. 2004; Brus et al. 2002), according to (e.g. De Vries et al. 2007b):

$$\log ctM_{plant,crit} = a_0 + a_1 \cdot pH_{KCl} + a_2 \cdot \log OM + a_3 \cdot \log clay + m \cdot \log ctM_{tot,crit} \quad (2.8)$$

where $ctM_{plant,crit}$ is the critical limit for metal concentration in plant (mg kg^{–1}) and m is a coefficient describing the non-linear relationship between the metal concentrations in plant and soil. Values for the various regression coefficients in Eq. (2.8) have been derived for Cd, Pb, Hg, Cu and Zn in grass, maize, sugar beet, wheat, potatoes, lettuce, endive and spinach (De Vries et al. 2008). The relationships obtained for Cd and Zn were much better than those for Pb, Hg and Cu. For the majority of crops, soil-plant relationships for Pb, Hg and Cu are not statistically significant and should therefore not be used. Furthermore, the critical limit of Zn related to phytotoxic effects by far exceeds the measured plant values in the database, which limits the application of the regression model (strong extrapolation). Critical soil concentrations related to food quality criteria are thus only relevant for Cd. Values for a_0 – a_3 and m for Cd, derived for Dutch soils, are given in Table 2.2. Examples of limits depending on soil type and pH for various crops are given in De Vries et al. (2007b).

The derivation of critical soil metal concentrations from acceptable daily intakes (ADI) by animals is relevant for grazing animals (specifically cows). Acceptable

Table 2.3 Overview of transfer functions to calculate K_f according to Eq. (2.11) with ctM_{tot} in mmol kg⁻¹ and $[M]_{tot}$ in mmol l⁻¹ and both *OM* and *clay* in % (Römkens et al. 2004)

Metal	b_0	b_1	b_2	b_3	n	R^2	se- y_{est} ^a
Cd	-4.85	0.27	0.58	0.28	0.54	0.79	0.33
Cu	-3.55	0.16	0.48	0.18	0.47	0.62	0.35
Pb	-2.96	0.25	0.83	0.02	0.68	0.57	0.55
Zn	-4.51	0.45	0.39	0.35	0.74	0.82	0.40

^a Standard error of the y-estimate on a logarithmic basis

daily intakes of metals can be related to critical metal contents in fodder (grass) and soil according to:

$$ADI = ctM_{plant,crit} \cdot I_{plant} + ctM_{tot,crit} \cdot I_{soil} \quad (2.9)$$

where *ADI* is acceptable daily intake of metals (mg d⁻¹); I_{plant} is intake of plants (fodder) (kg d⁻¹) and I_{soil} is intake of soil (kg d⁻¹). The critical soil metal concentration can be derived by combining Eq. (2.8) and (2.9) and solving for $ctM_{tot,crit}$ using a given ADI and given coefficients in the soil-plant relationship (see Table 2.2 for grass). As with food quality criteria for plants, the derivation of a critical soil metal concentration from ADI values is mainly relevant for Cd. Information on the derivation of ADI values for Cd, using food quality criteria for Cd in the kidney of cows, and data on the intake of plants and soil are given in De Vries et al. (2007b).

Critical concentrations for the total metal concentration in soil solution, $[M]_{tot}$, that are ultimately needed in a critical load calculation, can then be derived from a relationship between the total metal concentration in soil and in soil solution, according to (Römkens et al. 2004):

$$ctM_{tot} = K_f \cdot [M]_{tot}^n \quad (2.10)$$

where K_f is the Freundlich adsorption constant, a function of soil properties such as pH, organic matter content and clay content, and n is an exponent. An example of a transfer function describing the adsorption constant K_f is (Römkens et al. 2004):

$$\log K_f = b_0 + b_1 \cdot pH_{extract} + b_2 \cdot \log OM + b_3 \cdot \log clay \quad (2.11)$$

Values for b_0 – b_3 and n for Cd, Cu, Pb and Zn, derived for Dutch soils, are given in Table 2.3. By using a critical limit for a metal in plants, a critical concentration in soil solution can thus be derived by a combination of Eq. (2.8, 2.10, and 2.11). A more involved way, often used in critical load calculations, is to use a relationship between: (i) the total metal content and reactive metal content, followed by (ii) a relationship between the reactive metal content and the free metal ion concentration (see e.g. Groenenberg et al. 2012) and then by (iii) a relationship between the free metal ion and total metal concentration in soil solution (e.g. De Vries and Groenenberg 2009).

2.3.2 *Aquatic Ecosystems*

2.3.2.1 Impacts of Metal Deposition

Concern about the input of metals to terrestrial ecosystems is also related to the ecotoxicological impact on aquatic organisms due to runoff to surface waters. Effects on aquatic organisms, including algae, crustacea and fish, include effects on gill function (Sola et al. 1995), nervous systems (Baatrup 1991), and growth and reproduction rates (Mance 1987). Human health effects of heavy metal uptake by consumption of aquatic organisms (fish) are specifically related to Hg (Meili 1997; Meili et al. 2003).

2.3.2.2 Critical Limits of Geochemical Indicators

Impacts of metals in aquatic ecosystems are related to contents in fish (this holds for Hg, for which a critical limit of 0.5 mg kg^{-1} fresh weight is used) and total dissolved metal concentrations (mg m^{-3} or $\mu\text{g l}^{-1}$) in surface water, being the relevant geochemical indicator for effects on aquatic organisms. Critical limits for metals in surface water are based on the OECD approach for calculating MPCs or critical limits of substances (OECD 1989) as presented in Sect. 2.3.1. Critical limits for total dissolved metal concentrations in surface water have been derived on the basis of chronic toxicity data for a variety of aquatic organisms, including the major taxonomic groups, i.e. algae, crustacea, macrophyta, molluscs and fish. A summary of effect-based critical limits, based on various EU Risk Assessment Reports for Cd, Pb, Cu, Zn and Hg, is presented in Table 2.4.

Values of the HC_5 are based on the 5th percentile cut-off value of various chronic toxicity data (Aldenberg and Slob 1993, Aldenberg and Jaworska 2000). For all metals, the HC_5 thus derived was divided by a so-called ‘assessment factor’ to assess the MPC. An assessment factor is a parameter that aims to calculate sufficiently ‘safe’ MPCs by accounting for e.g.: (i) limited endpoints covered, (ii) limited diversity and representativity of the taxonomic groups covered, (iii) statistical uncertainties around the 5th percentile estimate and (iv) limited validation of the HC_5 with multi-species mesocosm or field data. The necessity of such a factor, varying from 1 to 4 for the various metals, can be disputed. A comparison between the critical dissolved concentrations derived for soil solution at high pH, and surface water (Table 2.4) shows that the critical concentration is generally much lower in surface waters than in the soil solution for Cd, Zn and Pb and comparable for Cu and Hg (De Vries et al. 2007b). The differences between soil and surface water critical limits can be questioned. There is no theoretical reason why the sensitivities of soil and water organisms to metals should not be similar, assuming that the uptake of the free ion from the aqueous phase is the significant mechanism leading to toxicity. More research is needed to study the possibility to use similar limits for surface waters and soil solution. To avoid the risk of adverse effects, one may use the lowest values in deriving a critical load.

Table 2.4 Recommended critical limits for dissolved total Cd, Pb, Hg, Cu and Zn concentrations in surface waters (based on various EU risk assessment reports as summarized in De Vries et al. (2007b))

Metal	Data sources	HC5 concentration (mg m ⁻³)	Assessment factor	Critical limit (mg m ⁻³)
Cd	168 single species studies 9 multi species studies	0.38	2	0.19
Pb	19 freshwater NOECs/EC10s 11 saltwater NOECs/EC10s	5.0	3	1.6
Hg	30 freshwater and saltwater NOECs/EC10s	0.142	4	0.036
Cu	22 freshwater species specific NOECs/EC10s 4 multi species studies	8.2	1	8.2
Zn	18 freshwater NOECs/EC10s	15.6	2	7.8

2.4 Impacts of Nitrogen Deposition on Terrestrial and Aquatic Ecosystems and Geochemical Risk Indicators

2.4.1 Terrestrial Ecosystems

2.4.1.1 Impacts of Nitrogen Deposition

Theory on Ecosystem Nitrogen Saturation: Aber et al. (1989) launched the theory on ecosystem N saturation, focused on forest ecosystems, in which different stages can be identified in view of: (i) impacts on soil chemical processes such as mineralization, immobilization, nitrification, affecting N leaching, (ii) plant nutrition and forest growth and (iii) plant species diversity. Until a certain threshold level is reached, terrestrial ecosystems will react to additional N inputs by an increased biomass production until a physiological optimum (which is beyond the ecological optimum), but above that, production stays constant or even decreases. Below the threshold level for growth, however, changes in the ecosystem are already observed, especially the plant species diversity may gradually change towards more nitrophilic species (Bobbink et al. 1998; Bobbink and Hettelingh 2011; Ellenberg 1985). These impacts are discussed in more detail in Chaps. 4 and 5. In terrestrial (forest) ecosystems with a continuous elevated N input, the ecosystem may approach “N saturation” (Aber et al. 1989). In this stage, N leaching will increase above (nearly negligible) background levels, associated with soil acidification in terms of elevated leaching of base cations or aluminium, causing a decrease in ANC. Aber et al. (1998) hypothesize that the loss of mycorrhizal assimilation and exudation “could be a key process leading to increased nitrification and nitrate mobility”. At the stage of “N saturation” or “N excess”, the ecosystem may be destabilised by

the interaction of a number of factors. It may cause nutrient imbalances, since the uptake of base cations (Ca, Mg, K) is reduced by increased levels of dissolved Al and NH_4 (Boxman et al. 1988). This effect may be aggravated in systems of low N status, where an elevated input of N will increase forest growth, thus causing an increased demand for base cations. Observations of increased tree growth of European forests (Spiecker et al. 1996) may be the effect of increased N inputs. An excess input of N can finally cause pollution of ground water due to high NO_3 leaching. An overview of possible effects on forests as a result of increased atmospheric acid and N deposition and/or exposure to air pollutants is presented by Erisman and De Vries (2000). An overview of impacts on ecosystem functions can also be found in Hettelingh et al. (2009) and De Vries et al. (2014) and in Chap. 24.

N deposition impacts on ecosystems can roughly be divided into the following categories: (i) direct toxicity of N gases and aerosols to individual species, (ii) eutrophication, (iii) acidification, (iv) differential effects of oxidised and reduced N, and (v) increased susceptibility to secondary stress and disturbance factors. An overview of the direct effect of nitrogenous gases and aerosols (NH_3 , NO_2 , NO , HNO_3 and NH_4^+) is summarized in the Annex, since direct effects and critical levels are not part of this book, while soil acidification effects have been described above. Below, we shortly elaborate on the other N-related effects.

Eutrophication: Increased N deposition results in an increase in the availability of inorganic N in the topsoil in the short term, except in bogs and fens. This gradually leads to an increase in plant productivity in N-limited vegetation, and thus to higher annual litter production and litter with high concentrations of N. Because of this, N mineralisation will also gradually increase, which, in turn, may increase plant productivity. This is a positive feedback, because higher N mineralisation leads to higher N uptake and its subsequent effects. Local plant species diversity increases with increasing resource availability when starting from originally very low levels. Above a certain level of primary productivity, however, local plant species diversity declines as production increases. Observational studies across N deposition gradients and many N-addition experiments demonstrate this effect in the long term. Competitive exclusion ('overshading') of characteristic species of oligotrophic or mesotrophic habitats occurs in the presence of relatively fast-growing nitrophilic species, with rare species at low abundances being especially at risk (e.g. Bobbink et al. 1998; Suding et al. 2005).

The rate of N cycling in the ecosystem clearly increases in case of high N inputs, although the response time to increased N inputs can be long in highly organic soils (with high C:N ratios), or, indeed in any soil with large potential N sinks. When N is no longer limiting in the ecosystem, plant growth becomes limited by other resources, such as phosphorus (P), K, Mg, or water. In this situation, the productivity of the vegetation does not increase further with continuing N input. However, N concentrations within the plants often tend to increase when N availability continues to increase and the increased N content may affect the palatability of the vegetation for herbivores or the sensitivity to pathogens. These processes will also affect the composition of microbial communities.

Differences in Effects of Oxidised Versus Reduced N: The response of sensitive plant species can be significantly affected by a change in N form. Species of calcareous or slightly acidic soils are able to use nitrate, or a combination of nitrate and ammonium, as their N source, whereas some studies showed that species in acidic habitats generally use ammonium (e.g. Gigon and Rorison 1972; Kinzel 1982). Laboratory and field studies demonstrate that the performance of most forest understory species of deciduous forests in southern Sweden improves when not only ammonium but also nitrate is available (Falkengren-Grerup et al. 1998; Olsson and Falkengren-Grerup 2000). One of the impacts of increased ammonium uptake is a reduced uptake of base cations (Ca, Mg and K) to the rhizosphere. Ultimately this can lead to severe nutritional imbalances (references in Bobbink et al. 2003, e.g. Nihlgård 1985; Van Dijk et al. 1990). High concentrations of ammonium in the soil solution are also toxic to many sensitive plant species, disrupting cell physiology, cell acidification, accumulation of N-rich amino acids, poor root development, and inhibition of shoot growth. Strong evidence exists that many endangered vascular plant species of grasslands, heathlands and soft-water lakes, and fen bryophytes, are very intolerant to increased concentrations of reduced N and to high $\text{NH}_4^+:\text{NO}_3^-$ ratios (De Graaf et al. 1998; Kleijn et al. 2008; Paulissen et al. 2004; Van den Berg et al. 2008). Kleijn et al. (2008) for example, showed that growth of rare species typical to Dutch heaths, mat grass swards and fen meadows occurs only at low $\text{NH}_4^+/\text{NO}_3^-$ ratios. Soil conditions (pH levels) were shown to severely affect toxicity levels of reduced N (Lucassen et al. 2003).

Increased Susceptibility to Secondary Stress and Disturbance Factors: Strong accumulation of N in foliage (e.g. as amino acids) may also affect frost hardiness and the intensity and frequency of insect and pathogenic pests. The sensitivity of plants to stress (defined here as external constraints, such as drought, frost, pathogens or herbivores, which limit dry-matter production), or disturbance factors (mechanisms which affect plant biomass by causing its partial or complete destruction), may be significantly affected by N deposition. With increasing N deposition, susceptibility to fungal pathogens and attacks by insects also increases. This is probably due to altered concentrations of phenolic compounds (leading to lower resistance) and soluble N compounds, such as free amino acids, in combination with a lower vitality of individual plants. Increased levels of pathogenic fungi have been found for several tree species in N-addition experiments and field surveys, but for most ecosystems data are lacking and the influence of such pathogens on diversity is still unclear (e.g. Bobbink et al. 2003; Flückiger et al. 2002).

In general, herbivory is affected by the palatability of plant material, which is strongly determined by its N content. Increased organic N content in plants, caused by N deposition, can thus result in increased insect herbivory (e.g. Throop and Lerdau 2004). Data on herbivory and N deposition are very scarce, but a link has been demonstrated in dry *Calluna* heathlands. The frequency and intensity of infestations of heather beetle (*Lochmaea suturalis*) are clearly related to atmospheric N inputs and N concentrations in the heather (e.g. Berdowski 1993; Brunsting and Heil 1985). N-related changes in plant physiology, phenology, biomass allocation

(root:shoot ratios) and mycorrhizal infection can also differentially influence the sensitivity of plant species to drought or frost stress, leading to reduced growth in some species and possible changes in plant interactions.

Enhanced N Availability: Enhanced N availability may also cause water stress as a result of increased canopy size, increased shoot/root ratio and loss of mycorrhizal activity. This is due to: (i) water shortage, since a high N input favours growth of canopy biomass, whereas root growth is relatively unaffected (De Visser 1994), (ii) nutrient imbalances, since the increase in canopy biomass also causes an increased demand of base cation nutrients (Ca, Mg, K) whereas the uptake of these cations is reduced by increased levels of dissolved NH_4 (Boxman and van Dijk 1988) and (iii) an increased sensitivity to natural stress factors such as frost (Aronsson 1980; Bruck 1985) and attacks by fungi (Roelofs et al. 1985).

2.4.1.2 Critical Limits of Geochemical Nitrogen Indicators

Critical Soil C/N Ratios in View of Enhanced N Leaching: One possible indicator for N eutrophication impacts is the C/N ratio of either the organic layer or the mineral soil. There are indications that N retention is reduced with a decreasing soil C/N ratio, especially in the organic layer, as shown by Dise et al. (1998a, b) and Gundersen et al. (1998). Gundersen et al. (1998) presented a very limited C/N range in organic layers (25–30) to distinguish sites with high N retention, and thus low N leaching potential (>30), from those with low N retention and thus high low N leaching potential (<25). MacDonald et al. (2002), using a so-called IFEF dataset of published N budgets and C/N ratios of the organic layer, found the strongest relationships between N output and N input when the data were divided into ‘N-rich’ sites ($\text{C/N} \leq 25$) and ‘C-rich’ sites ($\text{C/N} > 25$). Using an updated IFEF dataset, Dise et al. (2009) found the strongest relationships between N output and N input when the data were also divided into ‘N-rich’ sites and ‘C-rich’ sites, but with a C/N in the organic layer of 23 as threshold value. De Vries et al. (2007a), using a so-called ICP Forests level-II dataset of 121 input-output budgets compiled with comparable methods within this Pan-European Forest Monitoring Programme, found less clear relationships with C/N. Their results showed that N leaching fluxes were negligible at very high C/N ratios in the organic layer (>35), but at lower C/N ratios the scatter in N leaching rates was very high, although N leaching tended to increase with a decrease in C/N ratio. Using a subset of this ICP Forests level II database, subjected to stringent quality control, Van der Salm et al. (2007) found that the highest explained variance in N leaching was found when including a positive relationship with temperature and an interaction between N throughfall and a critical C/N ratio of 23. The critical C/N ratio of 23, which is in line with results by Dise et al. (2009), was obtained by repetitive regression with different critical values. Considering the limited statistical relationship between soil C/N and N output one may argue that a C/N ratio in the organic layer between 20 and 25 is critical. From a dynamic point of view, one may argue that the C/N ratio should stay constant, as any lowering

Table 2.5 Acceptable N concentrations in soil solution given in the Mapping Manual (www.icpmapping.org), derived in De Vries et al. (2007c)

Impact	Critical N concentration (mg N l ⁻¹)
<i>Vegetation changes in Northern Europe^a</i>	
Lichens to cranberry	0.2–0.4
Cranberry to blueberry	0.4–0.6
Blueberry to grass	1–2
Grass to herbs	3–5
<i>Vegetation changes in Western Europe</i>	
Coniferous forest	2.5–4
Deciduous forest	3.5–6.5
Grass lands	3
Heath lands	3–6
<i>Other impacts on forests</i>	
Nutrient imbalances	(0.2–0.4) ^a
Elevated nitrogen leaching/N saturation	1
Fine root biomass/root length	1–3
Sensitivity to frost and fungal diseases	3–5

^a Note that these critical limits are not really substantiated by field observations (see main text)

leads potentially to an increase in N leaching. Since there is a very limited linkage between N output and C/N ratio without considering the N input, it is hardly used as a criterion in critical load calculations.

Critical Dissolved N Concentrations in View of Various Adverse Impacts: The main indicator for N impacts used in critical load assessments is the total inorganic N concentration in soil solution. This section includes a substantiation of reported critical limits summarized in Table 2.5, details of which can be found in De Vries et al. (2007c). The values have also been incorporated in the Mapping Manual (www.icpmapping.org).

Vegetation Changes: Critical limits for dissolved N concentrations in view of vegetation changes vary from 0.2–6.5 mg l⁻¹. The origin for the limits related to vegetation changes in Northern Europe (Table 2.5) is based on Warfvinge et al. (1992), who states that “limiting N soil solution concentrations have been suggested based on preliminary experiences from the Swedish Forest Survey program”. As shown by De Vries et al. (2007c), the values are based on an inverse use of the SMB model, by using empirically derived critical N loads and deriving the critical N leaching rate by subtracting values for the related N uptake, N immobilization and denitrification and dividing this flux by the water flux. These authors noted that the numbers may lack sufficient experimental ground truth, since it is the increase in N availability through enhanced N cycling that triggers vegetation changes and not the leaching of N. The origin for the limits related to vegetation changes in Western Europe (Table 2.5) is based on application of the biodiversity impact model NTM in

the Netherlands, indicating a range in median critical N concentration in soil solution of 0.1–5 mg l⁻¹ for grass lands and heath lands and of 0.1–10 mg l⁻¹ for forests, with a median value near 3 mg l⁻¹ (De Vries et al. 2007c).

Note that an application of critical N concentrations in the given intervals may lead to critical loads that are outside the range of empirical data on vegetation changes. In this case it is relevant to limit the critical loads to either the lowest or highest value of the encountered range in empirical critical loads (see Chaps. 4 and 5).

Nutrient Imbalances: The Mapping Manual (www.icpmapping.org) gives in brackets critical limits in view of nutrient imbalances that vary from 0.2–0.4 mg l⁻¹. These values are based on the assumption that an imbalance occurs as soon as N leaching exceeds natural N leaching rates. There is, however, no substantiation for this assumption, neither from the literature nor by the concepts of plant physiology. Nutrient imbalance has been assumed to occur when the availability of base cations (Ca, Mg and K) instead of N becomes limiting for growth, but this is not clearly related to a critical N concentration in soil solution (De Vries et al. 2007c).

N Leaching and Ground Water Quality: De Vries et al. (2007c) suggest an upper limit of 1 mg N l⁻¹ as differentiation between undisturbed and ‘leaky’ N saturated forest sites, based on Gundersen et al. (2006). These authors gave an overview of current water quality in forests by compiling a list of studies from the 1990s on nitrate concentration in seepage water from temperate forests, including >500 sites of seepage water from Europe. From the survey data it is difficult to conclude exactly at which level a forest ecosystem can be considered ‘leaky’, but they suggest an annual average N concentration level of 1 mg N l⁻¹ for seepage water and 0.5 mg N l⁻¹ for streams/catchments. Stoddard (1994) characterised four progressive stages of N saturation based on changes in seasonality and levels of nitrate leaching in streams and a value of 1 mg N l⁻¹ coincides with his limit for the near final stage. It is clear that the value for a leaking site is still far below the critical limits for ground water. The EC critical limit for NO₃-N in drinking water is 11.3 mg N l⁻¹ and the target value is 5.6 mg N l⁻¹.

Root Growth and Sensitivity to Frost and Diseases: Empirical data suggest that critical dissolved N concentrations in view of adverse impacts on fine root biomass/root length and an increased sensitivity to frost and fungal diseases vary between 1–3 mg N l⁻¹ and 3–5 mg N l⁻¹, respectively (De Vries et al. 2007c). The critical values for impacts on fine root biomass and root length are based on Matzner and Murach (1995), who found that total fine root biomass of Norway spruce saplings decreased significantly when the dissolved N (NO₃ + NH₄) concentration was >2 mg N l⁻¹. Critical dissolved N concentrations in view of an increased sensitivity to frost and fungal diseases has been derived from a critical N concentration in the needles of 18 g kg⁻¹, above which this sensitivity increases. De Vries et al. (2007c) derived a relationship between foliar N contents and dissolved annual average N concentrations on the basis of the results for 120 Intensive Monitoring plots in Europe. Below 3 mg N l⁻¹, the N contents in foliage were always below 18 g kg⁻¹, while above 5 mg N l⁻¹ values were nearly always above this value.

2.4.2 Aquatic Ecosystems

2.4.2.1 Impacts of Nitrogen Deposition

Eutrophication of Nutrient-Poor Aquatic Ecosystems: N deposition in natural ecosystems can lead to enhanced leaching of inorganic N from soils to surface waters, in cases where the supply of N is greater than plant and microbial demand, referred to as 'nitrogen saturation' (Aber et al. 1989; Stoddard 1994). In natural ecosystems, inorganic N species leached to surface waters are predominantly in the form of nitrate (NO_3). Effects of N leaching on surface water eutrophication were not considered likely until recently, because of P limitation of primary productivity (Stoddard 1994). Any additional N in a P-limited system could thus not be expected to stimulate algal growth. P limitation of primary productivity in surface waters has been the dominating view since the 1970s (Hecky and Kilham 1988; Schindler 1971, 1977). This view has been challenged recently in reviews (Elser et al. 2007; Lewis and Wurtsbaugh 2008; Sterner 2008), although earlier papers also stressed that N availability was important for algal production (Elser et al. 1990; Kratzer and Brezonik 1981).

An overview of literature concerning effects of N enrichment on the biology in nutrient-poor aquatic ecosystems in arctic, boreal and temperate regions is given in De Wit and Lindholm (2010). The choice for nutrient-poor ecosystems was guided by the focus under the LRTAP Convention on natural ecosystems, where local pollution sources (e.g. domestic sewage, industrial waste water, agriculture, etc.) are absent. Thus, any ecosystem responses to N will be most likely related to atmospheric N. Effects of N on freshwater systems were documented from various types of studies: historical records of lake sediments (paleolimnology), lake surveys and experimental studies focusing on algae (free-floating phytoplankton and sediment-dwelling benthic algae), water plants (macrophytes) and invertebrates (insects, snails).

Paleolimnological Evidence for N-Limitation: Lake sediment studies (paleolimnology) show shifts in algal communities and increases in algal growth related to higher N concentrations (Baron et al. 2009; Hobbs et al. 2010; Holmgren et al. 2009; Pla et al. 2009; Saros et al. 2003; Wolfe et al. 2001, 2006). Most paleolimnological papers on possible effects of N enrichment on phytoplankton communities in oligotrophic lakes are studies published from 2000 onwards. The studies have a wide geographical and climatic range and include temperate, alpine and arctic lakes from Europe and North-America, with N deposition levels between <1 and $>10 \text{ kg N ha}^{-1}\text{yr}^{-1}$. The changes in community structures are in varying degrees attributed to N enrichment (Baron et al. 2000; Wolfe et al. 2001) or to interactions of climate and N deposition (Hobbs et al. 2010; Holmgren et al. 2009; Pla et al. 2009; Saros et al. 2003; Wolfe et al. 2006). There are also shifts in paleolimnological records that are attributed to climate only (Birks et al. 2004; Ruhland et al. 2008). The evidence presented support the hypothesis that N deposition increases algal productivity and

can change algal community structure in oligotrophic arctic, alpine and temperate lakes, at levels of N deposition as low as <1 to $3 \text{ kg N ha}^{-1}\text{yr}^{-1}$, but especially in lakes receiving higher loads of atmospheric N ($>10 \text{ kg N ha}^{-1}\text{yr}^{-1}$). However, not all studies show evidence of higher productivity related to increased N, and some changes in community structure are interpreted as climate effects rather than N enrichment effects. As geochemical risk indicator, depletion of stable ^{15}N isotopes was used to infer enrichment of sediments by airborne N pollution.

Experiments and Surveys Supplying Evidence for N Limitation: Whole-lake experiments, mesocosms and bioassays are accepted methods used to experimentally investigate nutrient controls on freshwater primary productivity, in declining order of ecological realism and costs. Lake surveys along various gradients (deposition, climate, vegetation cover) are also used to statistically relate water chemistry and indicators of algal growth. In many studies a combination of some or all of these methods is used to gain insights in nutrient controls on productivity.

Whole-lake manipulations have often been done by manipulating both N and P supply (Fee 1979; Schindler 1977), and conflicting interpretations exist with respect to whether N limitation has been detected (Fee 1979; Schindler 1977; Schindler et al. 2008; Scott and McCarthy 2010). However, increases in productivity of both phytoplankton and sediment-dwelling algae were observed (Axler and Reuter 1996; Jansson et al. 2001) where only N was added, and several authors interpret results from lakes receiving both N and P as showing evidence of N-limitation, in addition to P-limitation and co-limitation (see also Finlay et al. 2013).

Regional surveys in boreal lakes in Europe and North America with N deposition between <1 and $>14 \text{ kg N ha}^{-1}\text{yr}^{-1}$ show higher chlorophyll concentrations per unit P in areas with higher N deposition, indicative of higher primary production (Bergström et al. 2005, 2008; Bergström and Jansson 2006). Experimental nutrient additions in lakes (mesocosm studies and bioassays) support the finding of the regional surveys by showing that co-limitation (N and P) or N limitation of algal growth is common, especially under conditions of low N availability (Andersson and Brunberg 2006; Lafrancois et al. 2004; Morris and Lewis 1988; Nydick et al. 2003, 2004; Saros et al. 2005). It is suggested that N deposition may have shifted primary productivity in oligotrophic lakes from N limitation to P limitation (Bergström and Jansson 2006; Elser et al. 2009).

2.4.2.2 Critical Limits of Geochemical Nitrogen Indicators

Critical limits of geochemical N indicators for eutrophication are not easy to quantify because effects do not depend on aqueous N concentrations only, but also on the availability of other nutrients. Lake chemistry, in combination with experimental evidence of impacts on phytoplankton, can be used to assess geochemical indicators for N limitation regarding phytoplankton. Total N to total P (TN:TP) mass ratios have been shown to correlate positively to N deposition in a large lake survey in Norway and Sweden (Elser et al. 2009). Nutrient enrichment studies in lakes in

Sweden, Norway and Colorado showed that N limitation occurred at TN:TP ratios below 20. However, some studies suggest that TN:TP ratios to evaluate nutrient deficiencies may underestimate N-deficiency, since total N in oligotrophic lakes is often partly unavailable (Axler et al. 1994; Maberly et al. 2002). Dissolved inorganic N (DIN) to TP ratios may be better predictors of responses to nutrient additions (Bergström 2010). Bergström (2010) evaluated the use of lake water concentration ratios as a geochemical indicator for N or P limitation of phytoplankton in oligotrophic lakes. The DIN:TP ratios correlated better with N limitation determined by bioassays than TN:TP ratios, and DIN:TP ratios were also better related to N deposition and catchment cover. For mass ratios of DIN:TP above 3.4, phytoplankton was usually P-limited, while N limitation dominated for a DIN:TP mass ratio below 1.5. For DIN:TP ratios between 1.5 and 3.4, co-limitation of N and P was common.

Camargo and Alonso (2006) performed a global assessment on the ecological and toxicological effects of inorganic N pollution in aquatic ecosystems. According to these authors, TN concentrations lower than 0.5–1.0 mg N l⁻¹ might prevent aquatic ecosystems from developing eutrophication and acidification. Most oligotrophic freshwaters have TN concentrations below this threshold (Elser et al. 2009), while impacts on phytoplankton productivity and communities still have been documented. Thus, several assessments underline the importance of using both N and P concentrations for evaluation of N effects on phytoplankton productivity, and highlight especially the use of DIN rather than TN. However, no consensus appears to have emerged regarding the threshold values for these ratios. The mass ratio of DIN:TP of 1.5 suggested by Bergström (2010), below which N limitation was common, could be used as a first approximation. Using of this limit implies that models calculating a critical N load for nutrient-poor freshwater ecosystems have to account for P-availability. Ratios of N:P in stream waters vary strongly with water discharge and its controls remain poorly understood (Green and Finlay 2010). Catchment retention of N is furthermore very variable depending on land cover, climate and N deposition. The present state of insights in these complex interactions implies that model based critical N loads in view of eutrophication are difficult to derive. Instead, empirical critical N loads have been derived for nutrient-poor aquatic systems, as presented in Chap. 4.

2.5 Overview of Critical Limits of Geochemical Indicators and Evaluation

Table 2.6 provides an overview of the relevant geochemical indicators for N, acidity and metals in soil and water (soil solution, ground water and surface water) with critical limits in view of their impacts on terrestrial and aquatic ecosystems.

A critical evaluation of each geochemical endpoint has been given above. In summary, the critical values related to ANC in view of effects on aquatic organisms (fish) are most clearly related to visible impacts in the field. Critical limits for Al, Bc/Al ratios and metals in soil solution, related to effects on soil organisms

Table 2.6 Geochemical indicators and typical critical limits used to derive critical loads for nitrogen, acidity and heavy metals

Aspect	Soil	Soil water/drinking water	Surface water
Acidity: Ecosystem effects	Reactive Al pool: no decrease	$[Al^{3+}]_{free} = 2 \text{ mg l}^{-1}$	ANC=20 (0–50) meq m^{-3} or ANC adjusted for TOC $[Al^{3+}] = 20 \text{ mg m}^{-3}$ to avoid impacts on roach
	Exchangeable BC pool/base saturation: no decrease	Molar $[Bc]/[Al] = 1$	pH=5.8 to avoid impacts on roach
Acidity: Human health effects		Indicator value of $[Al]_{tot}$ of $0.2 \text{ } \mu\text{g l}^{-1}$ to protect drinking water	
Metals: Ecosystem effects (Cd, Pb, Hg, Cu and Zn)	Total and reactive metal concentration (M_{tot} , M_{re})=function of pH, clay and organic matter content	$[M]_{free}$ = function of pH $[M]_{tot}$ = function of pH, solution chemistry and DOM	$[M]_{tot}$ in mg m^{-3} =0.19 for Cd, 1.6 for Pb, 0.036 for Hg, 8.2 for Cu and 7.8 for Zn
Metals: Human health effects (Cd, Pb, Hg)	Total Cd concentration = function of pH, clay and organic matter content; based on food quality criterion (0.1 mg kg^{-1} fresh weight) and soil plant relationship	$[Cd]_{tot}$, $[Pb]_{tot}$ and $[Hg]_{tot}$ of 3, 10 and $1 \text{ } \mu\text{g l}^{-1}$ to protect drinking water $[Cd]_{tot}$ = function of pH, clay and organic matter content; based on food quality criterion, soil plant relationship and soil solution relationship	$[Hg]_{tot}$ in fish = 0.5 mg kg^{-1} fresh weight
Nitrogen ecosystem effects	C/N ratio: no critical limit; Should not decrease to avoid N saturation	$[N]$ = function of type of impact as shown in Table 2.5: varies from $0.2\text{--}6 \text{ mg N l}^{-1}$	$[N] = 0.5\text{--}1.0 \text{ mg N l}^{-1}$ DIN:TP=1.5
Nitrogen: Human health effects		$[NO_3] = 50 \text{ mg l}^{-1}$ implying $[NO_3 - N] = 11.3 \text{ mg N l}^{-1}$ to protect drinking water	

and plants, are based on a harmonized methodology, but mostly based on laboratory experiments. Consequently, the linkage between exceedances of critical limits and field effects is limited, and exceedances thus only serve as a risk indicator for terrestrial ecosystems in view of possible long-term chronic effects. Critical metals limits related to human health effects are based on acceptable daily intakes and models that assess related critical limits for food crops, drinking water and fish, using a precautionary principle. Critical limits for N in soil solution and surface water

are mainly based on correlative studies under field conditions, but the impact is less clear than for ANC, amongst other due to interactions with phosphorus. Considering the above, field effects increase in probability going from acidification effects on terrestrial systems to eutrophication effects on terrestrial and aquatic systems to acidification effects on aquatic systems.

Uncertainties in the relation between critical chemical values and 'harmful effects' imply an associated uncertainty in the calculation of critical loads and their exceedances by atmospheric depositions. However, their influence on the robustness of 'risk' assessments, in the context described above, can be limited when moving from site-specific to regional model applications and from short to long time horizons (see, e.g., Chap. 25). All critical limits serve in critical load calculations and dynamic model calculations to enable standardized assessments on broad regional and temporal scales of the risks of atmospheric deposition to chosen end-points for structure and function of sensitive ecosystems indicators. The violation of a critical limit points to a risk of field effects that may vary over temporal and spatial scales. In general, the 'risk' associated with an exceedance of a critical limit implies an increased probability of occurrence of adverse effects, either now or in the future.

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