



Interim Report on Modelling Technology

**CCE ECOSYSTEMS IMPACT ASSESSMENT
METHODOLOGY (CCE-EIA)**

European Consortium for Modelling of Air Pollution and Climate
Strategies - EC4MACS
Task 3: Ecosystems Impact Assessment

Prepared by:

**Coordination Centre for Effects
at The Netherlands Environmental Assessment Agency
Bilthoven, The Netherlands.**

June 2008

CCE ECOSYSTEM IMPACT ASSESSMENT METHODOLOGY: CRITICAL LOADS AND DYNAMIC MODELLING

Coordination Centre for Effects (CCE)

This report gives an overview of the (potential) use of critical loads and dynamic model results in integrated assessment under EC4MACS and the LRTAP Convention. The main purpose of the report is to summarise the methods used to compute critical loads and their exceedances and to give an overview of the use of dynamic models.

Methods for calculating critical loads and their exceedances have been developed under the ICP Modelling and Mapping over the years and are published in the CCE Status Reports (see, e.g., Posch et al. 1993, 1995, 1997, 1999, 2001, 2003) and reprinted in the Mapping Manual (UBA 2004). Here we describe the methods for calculation critical loads of nutrient nitrogen and acidity for terrestrial ecosystems.

The motivation for dynamic modelling as well as a summary of the most commonly used models can be found in Posch et al. (2003b) and the Mapping Manual. The widely used Very Simple Dynamic (VSD) model is described in Posch and Reinds (2008).

1. Use of the CCE Environmental Impact Assessment methodology under EC4MACS and the LRTAP Convention

The objective of the CCE Environmental Impact Assessment (CCE-EIA) methodology in the context of EC4MACS is to assess impacts to the environment of the abatement of emissions of acidifying and eutrophying pollutants. The CCE-Environmental Impact Assessment (CCE-EIA) methodology establishes protection levels for nature against adverse effects (acidification and eutrophication) of air pollution for natural ecosystems in European countries. These protection levels are called “critical loads”. They have been computed to establish acceptable levels of the deposition of acidifying and eutrophying compounds.

Critical loads have been computed using a model (see chapter 2) and input-data that have been submitted by a network of collaborating national institutions (National Focal Centres). For countries that do not collaborate in the CCE network, critical loads are derived from established soil and vegetation databases. Critical loads have successfully been applied in combination with integrated assessment models such as RAINS to support European agreements for the abatement of the emissions of acidifying and nutrient nitrogen compounds (see also Hettelingh *et al.*, 1995; 2001; 2007).

The basic principle in these applications consists of comparing computed critical loads for European ecosystems (more than 1 million data points in natural areas in Europe) to ecosystem specific deposition. The spatial distribution of natural areas at risk, i.e. areas where depositions is higher than computed critical loads, is then used as side-constraint in RAINS or GAINS for the optimization of the distribution and magnitude of country emissions.

However, knowledge of biological effects of these so-called “exceedances” (see chapter 3) is limited as these vary as function of a number of elements including soil type, meteorology, land use and species occurrence. This is especially important from the point of view of risks caused by excessive deposition of nitrogen. The risk of nitrogen inputs in the environment is increasing and recently well documented (Galloway *et al.*, 2008).

Therefore, an important new focus of the use of CCE-EIA under EC4MACS is on the change of biodiversity caused by the deposition of nitrogen compounds. Knowledge under EC4MACS of impacts of nitrogen deposition to European natural areas that are classified under the European Nature Information System (EUNIS) is still developing and now also includes Natura2000 areas. For this the CCE is collaborating in the field of modelling dynamics of soil chemistry (see chapter 4) and of vegetation changes (see de Vries *et al.*, 2007). While progress in the dynamic modelling of soil chemistry is now well established especially with respect to acidification (see chapter 4) less progress has been made with the dynamic modelling of vegetation changes caused by nitrogen deposition. The regional assessment in Europe of the change of biodiversity due to nitrogen based air pollution is still subject to research that is data intensive. The uncertainties are still important.

Despite the lack of operational vegetation models on a European scale, improved knowledge is urgently required of the relationship between excessive nitrogen deposition and effects on biodiversity in Europe. Therefore, under EC4MACS, the CCE has extended the European application of computed critical loads to also include so-called empirical critical loads (see chapter 2.3 and Table 2-10) of nutrient nitrogen. Empirical critical loads are not based on mathematical models but on nitrogen addition experiments both in the field and in the laboratory (Achermann and Bobbink, 2003). The relationship between the exceedance of empirical critical loads and effects to vegetation (see Table 2-10) can be applied and mapped over European ecosystems, that have been classified under EUNIS.

The CCE is currently also exploring applications - on EUNIS regions in Europe - of relationships between nitrogen doses and impacts on the species richness. The European wide tentative application of dose-response curves is planned to become an element of the CCE-EIA methodology.

Therefore, the CCE Environmental Impact Assessment methodology can be summarized in a way that is schematically illustrated in Figure 1-1. Two kinds of critical loads, i.e. computed and empirical critical loads are available to identify European regions which are at risk due to emission reduction alternatives that are simulated under GAINS scenarios. The availability of two kinds of critical loads is used in a method called Ensemble Assessment of Impacts to establish the likeliness of the distribution of exceedances over European ecosystems. The Ensemble Assessment of Impacts methodology is developed under EC4MACS and has been documented in CCE Progress report 2007 (Slootweg *et al.*, 2007).

In addition, impacts of changes in exceedances to biological and bio-geochemical endpoints can be further analysed in terms of (a) the dynamics of bio-geochemistry (using dynamic models) and (b) impacts to species richness (using dose-response curves). The latter two kinds of endpoint assessments can be used to extend application possibilities of the Ensemble Assessment of Impacts in GAINS scenario analysis of impacts (see Figure 1.1.)

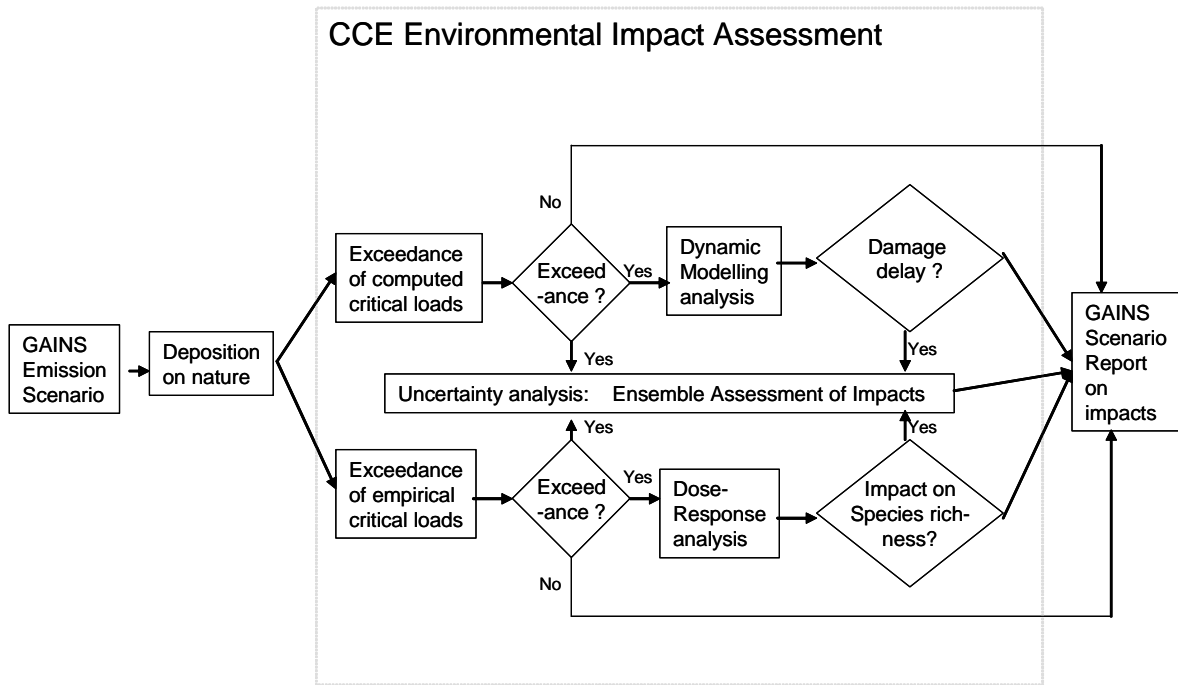


Figure 1-1 Schematic overview of the CCE Environmental Impact Assessment (CCE-EIA) methodology in the context of EC4MACS for the analysis and comparison of impacts relative to GAINS scenarios.

2. Modelling Critical Loads

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

In the following we consider only steady-state models, and we concentrate on the so-called Simple Mass Balance model for calculating critical loads for terrestrial ecosystems (Sverdrup et al. 1990, Sverdrup and De Vries 1994). Critical loads for aquatic ecosystems are provided by only a few countries. They are mostly calculated with the First-order Acidity Balance (FAB) model and the methods are summarised in Henriksen and Posch (2001), the Mapping Manual (UBA 2004) and an extension is described in Posch et al. (2007).

The Simple Mass Balance (SMB) model is a single-layer model, i.e. the soil is treated as a single homogeneous compartment. Furthermore, it is assumed that the soil depth is (at least) the depth of the rooting zone, which allows us to neglect the nutrient cycle and to deal with net growth uptake only. Additional simplifying assumptions include:

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

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

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

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

2.1 Critical loads of nutrient nitrogen (eutrophication)

2.1.1 Model derivation

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

$$(2.1) \quad N_{dep} + N_{fix} = N_{ad} + N_i + N_u + N_{de} + N_{eros} + N_{fire} + N_{vol} + N_{le}$$

where:

- N_{dep} = total N deposition
- N_{fix} = N ‘input’ by biological fixation
- N_{ad} = N adsorption
- N_i = long-term net immobilisation of N in soil organic matter
- N_u = net removal of N in harvested vegetation and animals
- N_{de} = flux of N to the atmosphere due to denitrification
- N_{eros} = N losses through erosion
- N_{fire} = N losses in smoke due to (wild or controlled) fires
- N_{vol} = N losses to the atmosphere via NH_3 volatilisation
- N_{le} = leaching of N below the root zone

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

The following assumptions lead to a simplification of eq.2.1:

- Nitrogen adsorption, e.g. the adsorption of NH_4 by clay minerals, can temporarily lead to an accumulation of N in the soil, however it is stored/released only when the deposition *changes*, and can thus be neglected in steady state considerations.
- Nitrogen fixation is negligible in most (forest) ecosystems, except for N-fixing species.
- The loss of N due to fire or burning (eg, forests, heather), erosion and volatilisation is small for most ecosystems in Europe, and therefore neglected in the following discussion. Alternatively, one can consider these terms included in the N_i -term, i.e. replace N_i by $N_i + N_{eros} + N_{fire} + N_{vol} - N_{fix}$ in all subsequent equations.
- The leaching of ammonium can be neglected in all forest ecosystems due to (preferential) uptake and complete nitrification within the root zone (i.e. $\text{NH}_{4,le} = 0$, $N_{le} = \text{NO}_{3,le}$).

Under these simplifying assumptions eq.2.1 becomes

$$(2.2) \quad N_{dep} = N_i + N_u + N_{de} + N_{le}$$

From this equation a critical load is obtained by defining an acceptable limit to the leaching of N, $N_{le(acc)}$, the choice of this limit depending on the “sensitive element of the environment” to be protected. If an acceptable leaching is inserted into eq.2.2, the deposition of N becomes the critical load of nutrient nitrogen, $CL_{nut}(N)$:

$$(2.3) \quad CL_{nut}(N) = N_i + N_u + N_{de} + N_{le(acc)}$$

In deriving the critical load of nutrient N as eq.2.3, it is assumed that the sources and sinks do not depend on the deposition of N. This is unlikely to be the case and thus all quantities should be taken ‘at critical load’. However, to compute, e.g., ‘denitrification at critical load’ one needs to know the critical load, the very quantity one wants to compute. The only clean way to avoid this circular reasoning is to establish a functional relationship between deposition and the sink of N, insert this function into eq.2.2 and solve for the deposition (to obtain the critical load). This has been done for denitrification: in the simplest case denitrification is linearly related to the net input of N (De Vries et al. 1993, 1994):

$$(2.4) \quad N_{de} = \begin{cases} f_{de} \cdot (N_{dep} - N_i - N_u) & \text{if } N_{dep} > N_i + N_u \\ 0 & \text{else} \end{cases}$$

where f_{de} ($0 \leq f_{de} < 1$) is the so-called denitrification fraction, a site-specific quantity. This formulation implicitly assumes that immobilisation and uptake are faster processes than denitrification. Inserting this expression for N_{de} into eq.2.2 and solving for the deposition leads to the following expression for the critical load of nutrient N:

$$(2.5) \quad CL_{nut}(N) = N_i + N_u + \frac{N_{le(acc)}}{1 - f_{de}}$$

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

More generally, it would be desirable to have deposition-dependent equations (models) for all N fluxes in the critical load equation. However, these either do not exist or are so involved that no (simple) explicit expression for $CL_{nut}(N)$ can be found. Although this does not matter in principle, it would reduce the appeal and widespread use of the critical load concept. Therefore, when calculating critical loads from eq.2.3 or eq.2.5, the N fluxes should be estimated as long-term averages derived from conditions not influenced by elevated anthropogenic N inputs.

2.1.2 The acceptable leaching of N

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

$$(2.6) \quad N_{le(acc)} = Q \cdot [N]_{acc}$$

where $[N]_{acc}$ is the acceptable N concentration (eq/m³) and Q is the precipitation surplus (in m³/ha/a). Some values for acceptable N concentrations are shown in Table 2-1.

Table 2-1: Acceptable N leachate concentrations to avoid nutrient imbalances or vegetation changes (Warfvinge et al. 1992; quoted from Posch et al. 1993).

Impact	$[N]_{acc}$ in mgN/L = gN/m ³	$[N]_{acc}$ in eq/m ³
Nutrient imbalance, conifers	0.2	0.0143
Nutrient imbalance, deciduous trees	0.2–0.4	0.0143–0.0276
Change lichens → cranberry	0.2–0.4	0.0143–0.0276
Change lingon → blueberry	0.4–0.6	0.0276–0.0429
Change blueberry → grass	1–2	0.0714–0.1429
Change grass → herbs	3–5	0.2143–0.3571

Although literature data indicate that nutrient imbalances may occur when N leaching increases above natural background values (Van Dam 1990), no direct relationship between N leaching and vegetation changes has been substantiated. In general, the low leaching values from the above table lead to critical loads that are lower than empirical data on vegetation changes (e.g. Bobbink et al. 1998). It is the increase in N availability through enhanced N cycling that triggers changes (Berendse et al. 1987).

An acceptable N leaching could also be derived with the objective to avoid N pollution of groundwater using, e.g., the EC target or limit value (25 and 50 mgN/L, resp.) as acceptable (but high!) concentration.

2.1.3 Sources and derivation of input data

The obvious sources of input data for calculating critical loads are measurements at the site under consideration. However, in many cases these will not be available. A discussion on all the N sources and sinks occurring in eq.2.1 can be found in Hornung et al. (1995) and UNECE (1995). Some data sources and default values, and procedures to derive them, are summarised in the following.

Nitrogen immobilisation:

N_i in the critical load equation refers to the long-term net immobilisation (accumulation) of N in the root zone, i.e. the continuous build-up of stable C-N-compounds in (forest) soils. In

other words, this immobilisation of N should not lead to significant changes in the prevailing C/N ratio. This has to be distinguished from the high amounts of N accumulated in the soils over many years (decades) due to the increased deposition of N, leading to a decrease in the C/N ratio in the topsoil.

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

Nitrogen uptake:

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

$$(2.7) \quad N_u = \frac{\text{N removed in harvested biomass (eq/ha)}}{\text{interval between harvests (rotation period)(yr)}}$$

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

$$(2.8) \quad N_u = k_{gr} \cdot \rho_{st} \cdot (ctN_{st} + f_{br,st} \cdot ctN_{br})$$

where k_{gr} is the average annual growth rate ($\text{m}^3/\text{ha}/\text{a}$), ρ_{st} is the density of stem wood (kg/m^3), ctN is the N content in stems (subscript st) and branches (subscript br) (eq/kg) and $f_{br,st}$ is the branch-to-stem ratio (kg/kg). The contribution of branches has to be neglected in case of stem removal only.

Values for the density of stem wood of most trees are in the range of 400–500 kg/m^3 for conifers and 550–700 kg/m^3 for deciduous trees. The branch-to-stem ration is about 0.15 kg/kg for conifers and 0.20 kg/kg for deciduous trees (Kimmins et al. 1985, De Vries et al. 1990). According to Swedish data (Rosén 1990; see also Reinds et al. 2001) the contents of N in stems are 1 g/kg for conifers and 1.5 g/kg in deciduous trees, whereas in branches of all tree species the N content is 4 g/kg in the south and 2 g/kg in the north. In a recent report Jacobsen et al. (2002) have summarised the results of a large number of studies on that subject, and Table 2-2 shows the average element contents in 4 major tree species, both for stems and branches. For N, the values have to be multiplied by $1/14=0.07143$ to obtain the N contents in eq/kg .

Table 2-2: Mean (and standard deviation) of the element contents (g/kg) in stems and branches (both incl. bark) of four tree species (Jacobsen et al. 2002; the number of data points ranges from 6 to 32).

Tree species	Contents (g/kg) in stems (incl. bark)				Contents (g/kg) in branches (incl. bark)			
	N	Ca ^{a)}	Mg	K	N	Ca	Mg	K
oak <i>quercus spp</i>	2.10 (0.46)	2.47 (1.42)	0.18 (0.07)	1.05 (0.51)	6.19 (1.02)	4.41 (0.65)	0.44 (0.14)	2.00 (0.47)
beech <i>fagus sylv.</i>	1.54 (0.25)	1.80 (1.12)	0.26 (0.09)	1.04 (0.13)	4.27 (1.36)	4.02 (1.91)	0.36 (0.13)	1.50 (0.44)
spruce <i>picea abies</i>	1.22 (0.49)	1.41 (0.40)	0.18 (0.06)	0.77 (0.43)	5.24 (1.66)	3.33 (1.06)	0.53 (0.27)	2.39 (1.35)
pine <i>pinus sylv.</i>	1.09 (0.30)	1.08 (0.30)	0.24 (0.09)	0.65 (0.28)	3.61 (1.28)	2.07 (0.65)	0.43 (0.11)	1.67 (0.68)

^{a)}Note that for Ca data points from calcareous sites are included in the statistics.

Growth rates used should be long-term average values, typical for the site. It has to be noted that recent growth rates are higher due to increased N input. Therefore it is recommended to use older investigations (yield tables), preferably from before 1960–70. Net uptake of N in non-forest natural and semi-natural ecosystems is insignificant, unless they are used for extensive grazing. For example, in the United Kingdom net removal of N in sheep (mutton/wool) due to extensive grazing is between 0.5 and 2.0 kgN/ha/a, depending on site fertility and grazing density.

Denitrification:

Dutch and Ineson (1990) reviewed data on rates of denitrification. Typical values of N_{de} for boreal and temperate ecosystems are in the range of 0.1–3.0 kgN/ha/a (=7.143–214.3 eq/ha/a), where the higher values apply to wet(ter) soils; rates for well drained soils are generally below 0.5 kgN/ha/a.

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

Table 2-3: Denitrification fraction f_{de} as function of the drainage status of the soil (Reinds et al. 2001).

Drainage status:	excessive	good	moderate	imperfect	poor	very poor
f_{de}	0	0.1	0.2	0.4	0.7	0.8

Other nitrogen sources and sinks:

N fixation may play an important role for some species, for example, the tree species red alder (Van Miegroet and Cole 1984).

For the N sources and sinks neglected in the above considerations, discussions and some data sources can be found in Hornung et al. (1995) and UNECE (1995).

Precipitation surplus:

The precipitation surplus Q is the amount of water percolating (vertically) through the root zone. It is conveniently calculated as the difference between precipitation and actual evapotranspiration and it should be the long-term climatic mean annual value. In many cases evapotranspiration will have to be calculated by a model using basic meteorological input data (precipitation, temperature, radiation etc.). For the basics of modelling evapotranspiration see, e.g., Monteith and Unsworth (1990) and for an extensive collection of models see Burman and Pochop (1994). Historical time series of meteorological data can be found, e.g., on the website

of the Climate Change Research Unit of the University of East Anglia (www.cru.uea.ac.uk/cru/data).

2.2 Critical loads of acidity

2.2.1 Model derivation: the Simple Mass Balance (SMB) equation

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

$$(2.9) \quad H_{le} + Al_{le} + BC_{le} + NH_{4,le} = SO_{4,le} + NO_{3,le} + Cl_{le} + HCO_{3,le} + RCOO_{le}$$

where the subscript *le* stands for leaching; *Al* stands for the sum of all positively charged aluminium species, *BC* is the sum of base cations ($BC = Ca + Mg + K + Na$) and *RCOO* is the sum of organic anions. A leaching term is given by $X_{le} = Q[X]$, where $[X]$ is the soil solution concentration of ion *X* and *Q* is the water percolating from the root zone (precipitation minus evapotranspiration). All fluxes are expressed in equivalents (moles of charge) per unit area and time (eq/ha/a). The concentrations of *OH* and *CO₃* are assumed zero, which is a reasonable assumption even for calcareous soils. The leaching of Acid Neutralising Capacity (ANC) is defined as:

$$(2.10) \quad ANC_{le} = HCO_{3,le} + RCOO_{le} - H_{le} - Al_{le}$$

Combination with eq.2.9 yields:

$$(2.11) \quad BC_{le} + NH_{4,le} - SO_{4,le} - NO_{3,le} - Cl_{le} = ANC_{le}$$

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

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

$$(2.12) \quad Cl_{le} = CL_{dep}$$

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

$$(2.13) \quad BC_{le} = BC_{dep} + BC_w - Bc_u$$

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

phenomenon, which cannot be taken into account when considering long-term steady-state conditions.

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

$$(2.14) \quad S_{le} = S_{dep} - S_{ad} - S_i - S_u - S_{re} - S_{pr}$$

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

$$(2.15) \quad SO_{4,le} = S_{dep}$$

For nitrogen, the mass balance in soil is (see Section 2.1):

$$(2.16) \quad N_{le} = N_{dep} + N_{fix} - N_{ad} - N_i - N_u - N_{de} - N_{eros} - N_{fire} - N_{vol}$$

where the subscripts *fix* refers to fixation of N, *de* to denitrification, and *eros*, *fire* and *vol* to the loss of N due to erosion, forest fires and volatilisation, respectively. N_i is the long-term immobilisation of N in the root zone, and N_u the net growth uptake (see BC_u above). Furthermore, the leaching of ammonium can be neglected in almost all forest ecosystems due to (preferential) uptake and complete nitrification within the root zone, i.e. $NH_{4,le}=0$. Under these various assumptions eq.2.16 simplifies to:

$$(2.17) \quad N_{le} = NO_{3,le} = N_{dep} - N_i - N_u - N_{de}$$

Inserting eqs.2.12, 2.13, 2.15 and 2.17 into eq.2.11 leads to the following simplified charge balance for the soil compartment:

$$(2.18) \quad S_{dep} + N_{dep} = BC_{dep} - Cl_{dep} + BC_w - BC_u + N_i + N_u + N_{de} - ANC_{le}$$

Strictly speaking, we should replace $NO_{3,le}$ in the charge balance not by the right-hand side of eq.2.17, but by $\max\{N_{dep}-N_i-N_u-N_{de},0\}$, since leaching cannot become negative; and the same holds true for base cations. However, this would lead to unwieldy critical load expressions; therefore we go ahead with eq.2.18, keeping this constraint in mind.

Since the aim of the LRTAP Convention is to reduce *anthropogenic* emissions of S and N, sea-salt derived sulphate should not be considered in the balance. To retain charge balance, this is achieved by applying a sea-salt correction to sulphate, chloride and base cations, using either Cl or Na as a tracer, i.e. the assumption that either all of the Cl or all of the Na deposition are sea-salt derived, respectively. Denoting sea-salt corrected depositions with a

star, one has either $Cl_{dep}^*=0$ or $Na_{dep}^*=0$ (and $BC_{dep}^*=BC_{dep}^*$), respectively. For procedures to compute sea-salt corrected depositions, see Appendix B in Posch et al. (2003).

For given values for the sources and sinks of S, N and base cations, eq.2.18 allows calculating the leaching of ANC, and thus assessing the acidification status of the soil. Conversely, critical loads of S and N can be computed by defining a critical ANC leaching, which is set to avoid ‘harmful effects’ on the ‘specified sensitive element of the environment’. Assuming a critical ANC leaching, $ANC_{le,crit}$, as given and using sea-salt corrected depositions, one obtains for the critical loads of sulphur, $CL(S)$, and acidifying nitrogen, $CL(N)$ from eq.2.18:

$$(2.19) \quad CL(S) + CL(N) = BC_{dep}^* - Cl_{dep}^* + BC_w - Bc_u + N_i + N_u + N_{de} - ANC_{le,crit}$$

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

$$(2.22) \quad CL_{max}(S) = BC_{dep}^* - Cl_{dep}^* + BC_w - Bc_u - ANC_{le,crit} = BC_{dep}^* - Cl_{dep}^* - Bc_u + CL(A)$$

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

$$(2.23) \quad N_{dep} \leq CL_{min}(N) = N_i + N_u + N_{de}$$

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

$$(2.24) \quad CL_{max}(N) = CL_{min}(N) + CL_{max}(S)$$

The three quantities $CL_{max}(S)$, $CL_{min}(N)$ and $CL_{max}(N)$ define the *critical load function* (depicted in Figure 2-1a): For every pair of deposition (N_{dep}, S_{dep}) lying on that function are critical loads of acidifying S and N.

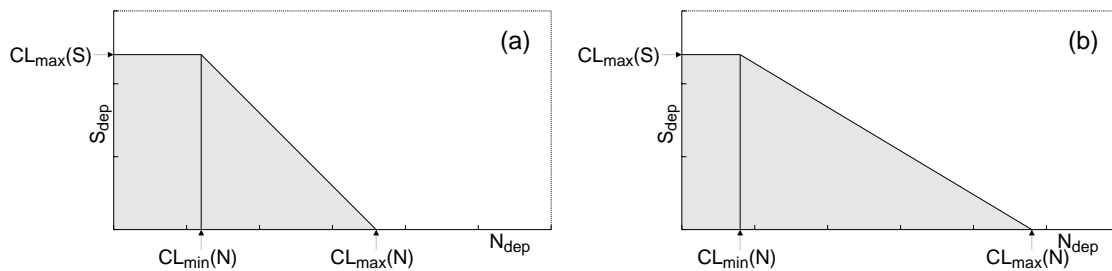


Figure 2-1: Critical load function of sulphur and acidifying nitrogen, defined by the three quantities $CL_{max}(S)$, $CL_{min}(N)$ and $CL_{max}(N)$. (a) with constant denitrification N_{de} , and thus a 45° slope of the CL function; (b) with deposition-dependent denitrification, resulting in a smaller $CL_{min}(N)$ and a flatter slope, depending on f_{de} . The grey area below the CL function denotes deposition pairs resulting in an ANC leaching smaller than $ANC_{le,crit}$ (non-exceedance of critical loads).

Deriving critical loads as above assumes that the sources and sinks of N do not depend on the N deposition. This is unlikely to be true; and as in Section 2.1 we consider also the case of denitrification being linearly related to the net input of N. Substituting eq.2.4 for N_{de} into the equations above results in the following expressions for $CL_{min}(N)$ and $CL_{max}(N)$:

$$(2.25) \quad CL_{min}(N) = N_i + N_u$$

and

$$(2.26) \quad CL_{max}(N) = CL_{min}(N) + \frac{CL_{max}(S)}{1 - f_{de}}$$

where f_{de} ($0 \leq f_{de} < 1$) is the denitrification fraction; $CL_{max}(S)$ remains the same (eq.2.22). An example of a critical load function with $f_{de} > 0$ is shown in Figure 2-1b.

2.2.2 Chemical criteria and the critical leaching of ANC

The leaching of Acid Neutralising Capacity (ANC) is defined in eq.10. In the simplest case bicarbonate (HCO_3) and organic anions (RCOO) are neglected since they do not contribute significantly at low pH values (but see below). In this case the ANC leaching is given by:

$$(2.27) \quad ANC_{le} = -H_{le} - Al_{le} = -Q \cdot ([H] + [Al])$$

where Q is the precipitation surplus in $\text{m}^3/\text{ha}/\text{a}$ (see Section 2.1 for data).

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

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

$$(2.28) \quad [Al] = K_{gibb} \cdot [H]^3 \quad \text{or} \quad [H] = ([Al] / K_{gibb})^{1/3}$$

where K_{gibb} is the gibbsite equilibrium constant (see below). Eq.2.28 is used to calculate the (critical) Al concentration from a given proton concentration, and *vice versa*.

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

Aluminium criteria

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

(a) Critical Al concentration:

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

$$(2.29) \quad ANC_{le,crit} = -Q \cdot \left(\left([Al]_{crit} / K_{gibb} \right)^{1/3} + [Al]_{crit} \right)$$

(b) *Critical base cation to aluminium ratio:*

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

The critical Al leaching is calculated from the leaching of base cations (compare eq.2.13):

$$(2.30) \quad Al_{le,crit} = 1.5 \cdot \frac{Bc_{le}}{(Bc/Al)_{crit}} = 1.5 \cdot \frac{Bc_{dep} + Bc_w - Bc_u}{(Bc/Al)_{crit}}$$

The factor 1.5 arises from the conversion of mols to equivalents (assuming that K is divalent). Using eqs.2.27 and 2.28, this yields for the critical ANC leaching:

$$(2.31) \quad ANC_{le,crit} = -Q^{2/3} \cdot \left(1.5 \cdot \frac{Bc_{dep} + Bc_w - Bc_u}{K_{gibb} \cdot (Bc/Al)_{crit}} \right)^{1/3} - 1.5 \cdot \frac{Bc_{dep} + Bc_w - Bc_u}{(Bc/Al)_{crit}}$$

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

Alternatively, if considered more appropriate, a critical molar ratio of calcium to aluminium in soil solution can be used, by replacing all the Bc -terms in eq.2.31 with Ca -terms.

(c) *Critical Al mobilisation rate:*

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

$$(2.32) \quad Al_{le,crit} = Al_w$$

where Al_w is the weathering of Al from primary minerals (eq/ha/a). The weathering of Al can be related to the base cation weathering via

$$(2.33) \quad Al_w = p \cdot BC_w$$

where p is the stoichiometric ratio of Al to BC weathering in primary minerals (eq/eq), with a default value of $p=2$ for typical mineralogy of Northern European soils (range: 1.5–3). The critical leaching of ANC becomes then:

$$(2.34) \quad ANC_{le,crit} = -Q^{2/3} \cdot \left(\frac{p \cdot BC_w}{K_{gibb}} \right)^{1/3} - p \cdot BC_w$$

Hydrogen ion criteria:

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

(a) *Critical pH:*

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

$$(2.35) \quad ANC_{le,crit} = -Q \cdot \left([H]_{crit} + K_{gibb} \cdot [H]_{crit}^3 \right)$$

(b) *Critical base cation to proton ratio:*

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

$$(2.36) \quad ANC_{le,crit} = 0.5 \cdot \frac{Bc_{dep} + Bc_w - Bc_u}{(Bc/H)_{crit}}$$

where the factor 0.5 comes from converting mols to equivalents. For organic soils the weathering in eq.2.36 will probably be negligible ($Bc_w=0$). Values suggested for $(Bc/H)_{crit}$ are expressed as multiples of $(Bc/Al)_{crit}$, ranging from 0.3 for deciduous trees and ground vegetation to 1 for spruce and pine (Sverdrup and Warfvinge 1993).

Critical base saturation

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

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

As an example, we consider the description of the exchange between H, Al and $Bc=Ca+Mg+K$ as implemented in the Very Simple Dynamic (VSD) model (see Posch and Reinds 2008). For both models the critical concentration $[H]_{crit}$ can be found as a solution of an equation of the type

$$(2.37) \quad A \cdot [H]_{crit}^p + B \cdot [H]_{crit} - C = 0$$

where the coefficients A , B , C and the exponent p are given in Table 2-4.

Table 2-4: Coefficients in eq.2.37 for the Gaines-Thomas and Gapon exchange model.

Exchange model	A	p	B	C
Gaines-Thomas	$K_{Alox} \cdot \sqrt{K_{AlBc} \cdot (E_{Bc,crit} / [Bc])^3}$	a	$\sqrt{K_{HBc} \cdot E_{Bc,crit} / [Bc]}$	$1 - E_{Bc,crit}$
Gapon	$K_{Alox}^{1/3} \cdot k_{AlBc} \cdot E_{Bc,crit} / \sqrt{[Bc]}$	a/3	$k_{HBc} \cdot E_{Bc,crit} / \sqrt{[Bc]}$	$1 - E_{Bc,crit}$

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

In general, the non-linear equation 2.37 will have to be solved numerically. Only for the Gapon model and the special case of the gibbsite equilibrium ($a=3$, $K_{Alox}=K_{gibb}$) eq.2.37 becomes a linear equation with the solution:

$$(2.38) \quad [H]_{crit} = K_{Gap} \cdot \sqrt{[Bc]} \cdot \left(\frac{1}{E_{Bc,crit}} - 1 \right) \quad \text{with} \quad K_{Gap} = \frac{1}{k_{HBc} + k_{AlBc} \cdot K_{gibb}^{1/3}}$$

where k_{HBc} and k_{AlBc} are the two (site-specific) selectivity coefficients describing cation exchange and $[Bc]=B_{Cle}/Q$ as above. $[Al]_{crit}$ is then computed from the gibbsite equilibrium (eq.2.28) and from that the critical ANC leaching can be obtained via eq.2.29. Values of selectivity coefficients for a range of (Dutch) soil types and combinations of exchangeable ions can be found in De Vries and Posch (2003).

In Figure 2-2 the critical ANC leaching is shown for a range of constants K_{Gap} . This range encompasses a wide range of values for the exchange constants. The figure shows that ANC leaching is very sensitive to low values of the critical base saturation.

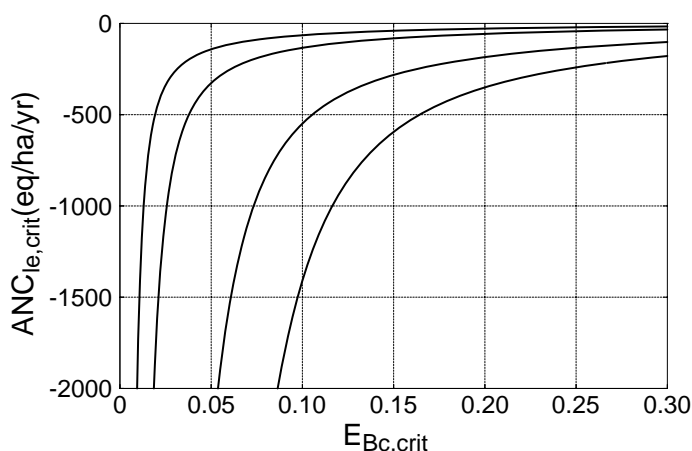


Figure 2-2: Critical ANC leaching (as defined by eq.2.27, for $Q=1$ m/a) as a function of the critical base saturation, $E_{Bc,crit}$ for $[Bc]=0.02$ eq/m³, $K_{gibb}=10^8$ and $K_{Gap}=0.005$ (leftmost curve), 0.01, 0.03 and 0.05 (rightmost curve). (To obtain $ANC_{Le,crit}$ for arbitrary Q , multiply the values on the vertical axis by Q in m/a; see also Figure 2-4 below.)

Base saturation is also used as criterion in the New England Governors/Eastern Canadian Premiers 'Acid Rain Action Plan' for calculating sustainable S and N depositions to upland forests with the SMB model (NEG/ECP 2001).

2.2.3 Sources and derivation of input data

The obvious sources of input data for calculating acidity critical loads are measurements at the site under consideration. However, in many cases these will not be available. For data on the

different N quantities see Section 2.1. Some data sources and default values for the other variables, and procedures to derive them, are summarised below.

Gibbsite equilibrium constant (K_{gibb}):

The equilibrium constant relating the Al concentration to pH (eq.2.28) depends on the soil. Table 2-5 presents ranges of K_{gibb} (and $pK_{gibb} = -\log_{10}(K_{gibb}$ in $(\text{mol/L})^{-2}$) as a function of the soil organic matter content. A widely used default value is $K_{gibb} = 10^8 (\text{mol/L})^{-2} = 300 \text{ m}^6/\text{eq}^2$.

Table 2-5: Ranges for K_{gibb} as a function of soil organic matter content.

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

If sufficient empirical data are available to derive the relationship between $[H]$ and $[Al]$, these should be used in preference to the gibbsite equilibrium (see Section 2.4).

Base cation and chloride deposition:

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

Base cation weathering:

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

(a) The Skokloster assignment:

This is a (semi-)empirical method devised at the Critical Loads Workshop at Skokloster (Sweden) (Table 1, p.40 in Nilsson and Grennfelt 1988). Details can be found in the section on empirical acidity critical loads (Section 2).

(b) The soil type – texture approximation:

Since mineralogy controls weathering rates, weathering rate classes were assigned to European (forest) soils by De Vries et al. (1993), based on texture class and parent material class. Texture classes are defined in Table 2-6 as a function of their clay and sand content:

Table 2-6: Soil texture classes as a function of their clay and sand content (Eurosoil 1999).

Texture class	Name	Definition
1	coarse	clay < 18 % and sand ≥ 65 %
2	medium	clay < 35% and sand > 15 %, but clay ≥ 18 % if sand ≥ 65 %
3	medium fine	clay < 35% and sand < 15 %
4	fine	35 % ≤ clay < 60 %
5	very fine	clay ≥ 60 %

Using the FAO soil classification (FAO 1981), the parent material class has been defined for each soil type in Table 2-7 (updated from De Vries 1993).

Table 2-7: Parent material classes for common FAO soil types (Posch et al. 2003).

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

Acidic : Sand(stone), gravel, granite, quartzine, gneiss (schist, shale, greywacke, glacial till)

Intermediate : Gronodiorite, loess, fluvial and marine sediments (schist, shale, greywacke, glacial till)

Basic : Gabbro, basalt, dolomite, volcanic deposits.

From texture and parent material class the weathering rate class is obtained from Table 2-8 (modified from De Vries 1993).

Table 2-8: Weathering rate classes as a function of texture and parent material classes (Posch et al. 2003).

Parent material	Texture class				
	1	2	3	4	5
Acidic	1	3	3	6	6
Intermediate	2	4	4	6	6
Basic	2	5	5	6	6
Organic	class 6 for Oe and class 1 for other organic soils				

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

$$(2.39) \quad BC_w = z \cdot 500 \cdot (WRc - 0.5) \cdot \exp\left(\frac{A}{281} - \frac{A}{273+T}\right)$$

where WRc is the weathering rate class (Table 2-8), T (°C) is the average annual (soil) temperature and $A=3600$ K (Sverdrup 1990). For calcareous soil, for which critical loads are not really of interest, one could set, e.g., $WRc=20$ in eq.2.39.

The above procedure provides weathering rates for $BC=Ca+Mg+K+Na$. However, for computing the critical ANC leaching according to eq.2.31, the weathering rate for $Bc=Ca+Mg+K$ is needed. Bc_w can be approximated by multiplying BC_w with a factor between 0.70 for poor sandy soils and 0.85 for rich (sandy) soils. Van der Salm (1998) (for texture classes 2–5, see Table 2-6) and De Vries (1994) (for texture class 1) provide regression equations for weathering rates of Ca, Mg, K and Na as a function of the sand (and silt) content of the soil, which can be used to split BC_w into individual weathering rates.

(c) *The total base cation content correlation:*

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

$$\begin{aligned}Ca_w &= 0.13 \cdot (Ca)_{tot} \cdot ETS - 55.5 \\(2.40) \quad Mg_w &= 0.23 \cdot (Mg)_{tot} \cdot ETS - 24.1 \\K_w &= 0.05 \cdot (K)_{tot} \cdot ETS - 79.8\end{aligned}$$

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

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

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

Weathering rates can be computed with the multi-layer steady-state model PROFILE (Warfvinge and Sverdrup 1992 and 1995). Basic input data are a total element analysis of the site, from which mineralogy is derived by a normative procedure. Generic weathering rates of each mineral are modified by the concentration of protons, base cations, aluminium and organic anions as well as the partial pressure of CO₂ and temperature. The total weathering rate is proportional to soil depth and the wetted surface area of all minerals present. For the theoretical foundations of this weathering rate model see Sverdrup (1990). For further information on the PROFILE model see www2.chemeng.lth.se.

(e) *Other methods:*

Weathering rates can also be estimated from budget studies of small catchments (see, e.g., Paces 1983). Be aware, however, that budget studies can easily overestimate weathering rates where there is significant cation release due to weathering of the bedrock. Other methods are listed and described in Sverdrup et al. (1990).

Base cation uptake:

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

The (long-term) net uptake of base cations is limited by their availability through deposition and weathering (neglecting the depletion of exchangeable base cations). Furthermore, base

cations will not be taken up below a certain concentration in soil solution, or due to other limiting factors, such a temperature. Thus the values entering critical load calculations have to be constrained by

$$(2.41) \quad Y_u \leq Y_{dep} + Y_w - Q \cdot [Y]_{min} \quad \text{for } Y = Ca, Mg, K$$

This is preferable to constraining the sum $Bc_u = Ca_u + Mg_u + K_u$ (see eq.2.31). Suggested values are 5 meq/m³ for $[Ca]_{min}$ and $[Mg]_{min}$, and zero for $[K]_{min}$ (Warfvinge and Sverdrup 1992). It should also be taken into account that vegetation takes up nutrients in fairly constant (vegetation-specific) ratios. Thus, when adjusting the uptake value for one element, the values for the other elements (including N) should be adjusted proportionally.

2.2.4 Possible extensions to the SMB

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

(a) Generalisation of the Al-H relationship:

In the SMB model the relationship between Al concentration and pH is described as a gibbsite equilibrium (see eq.2.21). However, Al concentrations, especially in the topsoil, are influenced by the complexation of Al with organic matter (Cronan et al. 1986, Mulder and Stein 1994). Therefore it is suggested to generalise the gibbsite equilibrium in the SMB model by

$$(2.42) \quad [Al] = K_{Alox} \cdot [H]^a$$

with equilibrium constant K_{Alox} and exponent a . Obviously, the gibbsite equilibrium is a special case of eq.2.42 (setting $a=3$ and $K_{Alox}=K_{gibb}$). The exponent a and K_{Alox} depend on the soil and especially on the soil horizon. As an example, in Table 2-9 values for K_{Alox} and a are presented for different soil groups and soil depths derived from data from about 350 Dutch forest stands (Van der Salm and De Vries 2001).

Table 2-9: Estimated values of K_{Alox} and the exponent a based on regression between pAl and pH in the solution of Dutch soils (Van der Salm and De Vries 2001) (n=number of samples).

Soil type	Depth (cm)	$\log_{10} K_{Alox}^a$	a	n
Sandy soils	0–10	-0.56	1.17	195
	10–30	2.37	1.88	348
	30–100	5.20	2.51	172
Peat	all depths	-1.06	1.31	116
Clay	all depths	7.88	2.65	116
Loess	0–10	-0.48	1.06	39
	10–30	3.29	1.90	39
	30–100	4.55	2.17	39

^aValues for K_{Alox} are derived from $[Al]$ and $[H]$ in mol/L; the unit of K_{Alox} depends on a and is (mol/L)^{1-a}.

The data in Table 2-9 show that a standard gibbsite equilibrium constant and $a=3$ is reasonable for clay soils. Very different values, however, are obtained for peat soils and, to a

lesser extent, also for sandy and loess soils (especially for shallow parts of the soil, where the organic matter content is highest).

Figure 2-3 shows the relationship between $[H]$ and $[Al]$ as well as its logarithmic form for different values of $K_{Al_{ox}}$ and a . If one defines $pX = -\log_{10}[X]$, with $[X]$ given in mol/L, then $pH = 3 - \log_{10}([H])$, if $[H]$ is expressed in eq/m^3 ; and for $[Al]$ in eq/m^3 the relationship is $pAl = 3 - \log_{10}([Al]/3)$. Empirical data from intensive forest monitoring plots show that there is a strong correlation between a and $pK_{Al_{ox}}$ (De Vries et al. 2003, p.118).

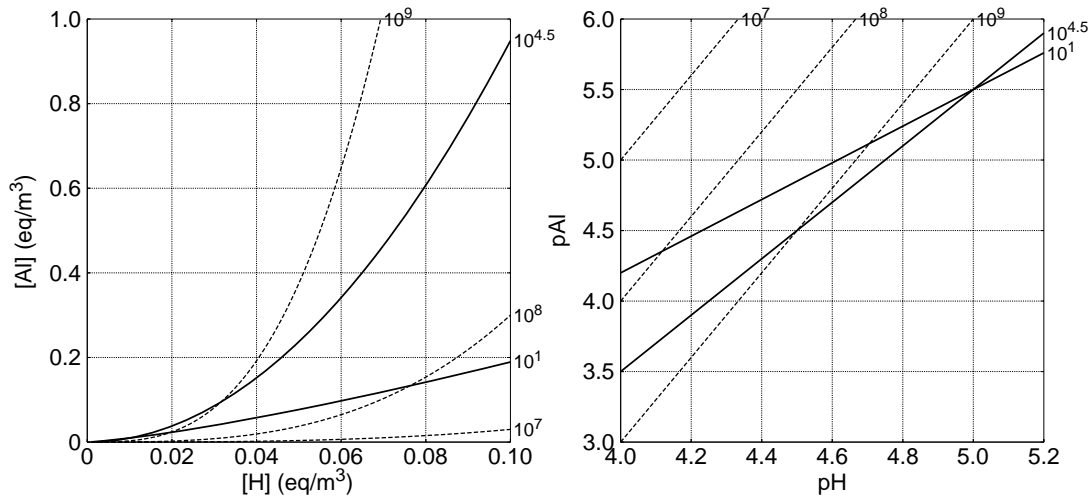


Figure 2-3: Relationships between proton and Al concentration in eq/m^3 (left) and in their logarithmic forms (right) for $K_{Al_{ox}} = 10^1$, $a=2$ and $K_{Al_{ox}} = 10^{4.5}$, $a=1.3$ (solid lines) as well as three gibbsite equilibria ($a=3$) with $K_{gibb} = 10^7$, 10^8 and 10^9 (dashed lines). Note: $[H] = 0.1 \text{ eq/m}^3$ corresponds to $pH = 4$.

Note that, when using eq.2.42 instead of eq.2.28, the formulae for $ANC_{le,crit}$ have to be adapted as well (mostly replacing the exponent 3 by a and $1/3$ by $1/a$).

(b) Including bicarbonate leaching:

The charge balance (eq.2.9) and the definition of ANC leaching in eq.2.10 also includes the leaching of bicarbonate anions ($HCO_{3,le} = Q \cdot [HCO_3]$). The concentration of bicarbonates is a function of the pH:

$$(2.43) \quad [HCO_3] = \frac{K_1 \cdot K_H \cdot p_{CO_2}}{[H]}$$

where K_1 is the first dissociation constant, K_H is Henry's constant and p_{CO_2} is the partial pressure of CO_2 in the soil solution (in atm). The two constants are weakly temperature-dependent, and the value for their product at 8°C is $K_1 \cdot K_H = 10^{-1.7} = 0.02 \text{ eq}^2/\text{m}^6/\text{atm}$.

For $p_{CO_2} = 0.0055 \text{ atm}$ (about 15 times the partial CO_2 pressure in air) and $Q = 0.3 \text{ m/a}$, eq.2.43 yields a bicarbonate leaching of almost 100 eq/ha/a at $pH = 5.5$, not always a negligible quantity. Therefore, it would make sense to include the bicarbonate leaching into the SMB model. Not only would this make critical loads more compatible with steady-state solutions of dynamic models, but it is also the only way to allow the ANC leaching to obtain positive values! Eq.2.27 would then read:

$$(2.44) \quad ANC_{le} = -H_{le} - Al_{le} + HCO_{3,le} = Q \cdot ([HCO_3] - [H] - [Al])$$

All chemical criteria could be used, since bicarbonate leaching could always be calculated from H_{le} via eq.2.43. We illustrate the influence of bicarbonates on the ANC leaching by re-drawing Figure 2-2, but now using eq.2.44 to calculate the ANC leaching. Comparing Figure 2-4 with Figure 2-2 illustrates that, depending on the parameters of the site, bicarbonate leaching can make a significant contribution to the overall ANC leaching.

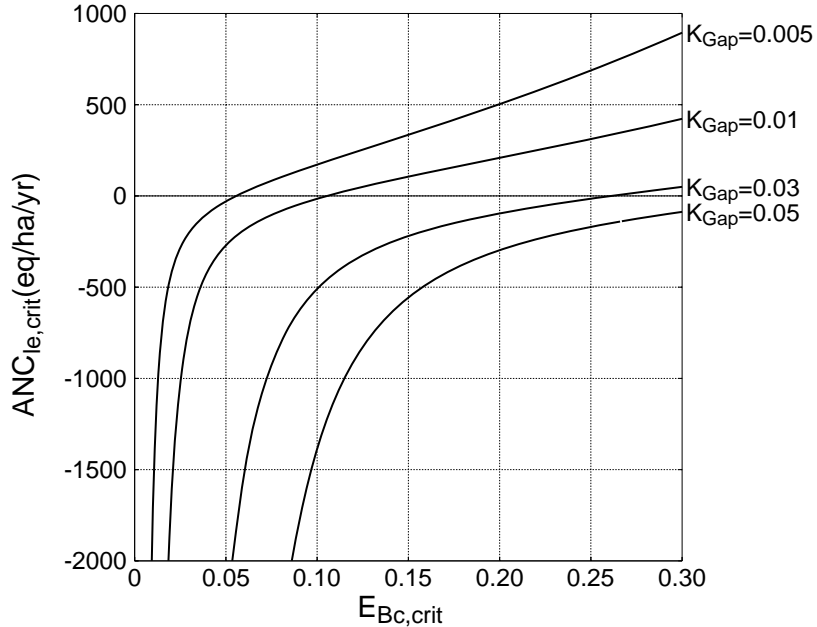


Figure 2-4: Critical ANC leaching (for $Q=1$ m/a) including bicarbonate leaching as a function of the critical base saturation, $E_{Bc,crit}$, using the same parameters as in Figure 2-2.

(c) Including the dissociation of organic acids:

The charge balance (eq.2.9) and the definition of ANC leaching in eq.2.10 also include the leaching of organic anions ($RCOO_{le}$). This has been neglected in the SMB model for (at least) two reasons: (i) to keep the SMB model simple, and/or (ii) assuming that the negatively charged organic anion concentration balances the positively charged organic Al-complexes. However, this does not hold for a wide range of pH values, and at sites with high concentrations of organic matter the contribution of organic anions to ANC leaching can be considerable.

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

$$(2.45) \quad [RCOO^-] = \frac{m \cdot DOC \cdot K_1}{K_1 + [H]}$$

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

Since a single value of K_1 does not always model the dissociation of organic acids satisfactorily, Oliver et al. (1983) have derived an empirical relationship between K_1 and pH:

$$(2.46) \quad pK_1 = -\log_{10} K_1 = a + b \cdot pH - c \cdot (pH)^2$$

with $a=0.96$, $b=0.90$ and $c=0.039$ (and $m=0.120$ mol/molC). Note that eq.2.46 gives K_1 in mol/L. In Figure 2-5 the fraction of $m\text{-DOC}$ dissociated as a function of pH is shown for the Oliver model and a mono-protic acid with a ‘widely-used’ value of $pK_1=4.5$.

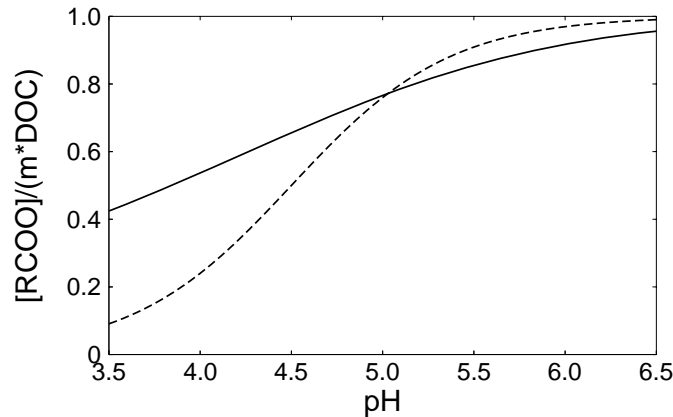


Figure 2-5: Fraction of organic acids ($m\text{-DOC}$) dissociated as a function of pH for the Oliver model (solid line) and the mono-protic model (eq.2.45) with $pK_1=4.5$ (dashed line).

Figure 2-5 shows that, depending on the amount of DOC, the contribution of organic anions to the ANC leaching, even at fairly low pH, can be considerable.

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

2.3 Empirical Critical Loads¹

Effects of nitrogen deposition are now recognised in nearly all oligotrophic natural ecosystems; these include aquatic habitats, forests, grasslands (including tundra and Mediterranean grasslands), oligotrophic wetlands (mire, bog and fen), heathland, and coastal and marine habitats (Achermann and Bobbink, 2003). An overview of major effects on plant species diversity, including impacts on mosses, lichens and mycorrhizae, for major terrestrial ecosystems in Europe (grasslands, heathland, coastal habitats wetlands and forests) is presented in **Error! Reference source not found.**-10. **Error! Reference source not found.**-10 also includes information on the related empirical critical N loads (see Achermann and Bobbink, 2003). In this approach, the critical load is the highest addition of nitrogen that does not lead to adverse physiological changes

¹ This paragraph draws on de Vries *et al.* (2007), a study commissioned and co-authored by the CCE. The report of this study can be downloaded from www.mnp.nl/cce.

(on the individual level) or loss in biodiversity (on the ecosystem level). In the approach, long-term (i.e., > 1 year) effects of nitrogen addition to existing vegetation play a central role. Such addition experiments are carried out in the field, or in the laboratory in so-called ‘mesocosms’ (i.e., pieces of vegetation directly taken from the field). Because of the time and labour-intensive nature of such studies, results are only available for a limited number of broadly defined ecosystems. In some cases, experimental results are supplemented by observational studies e.g. time series under a known increase in deposition (see de Vries *et al.* 2007 for further details on effects of nitrogen)

Table 2-10: Indicators for the effects of elevated N deposition and empirical critical loads ($\text{kg N ha}^{-1}\text{a}^{-1}$) for major ecosystem types (EUNIS classification) occurring in Europe (From Achermann and Bobbink, 2003)

Ecosystem type (EUNIS class)	EUNIS- code	Effect indicators	Empirical critical load
<i>Forest habitats (G)</i>			
Mycorrhizae	-	Reduced sporocarp production, reduced belowground species composition	10-20
Ground vegetation	-	Changed species composition, increased nitrophilous species; increased susceptibility to parasites (insects, fungi, virus)	10-15
Lichens and algae	-	Increase of algae; decrease of lichens	10-15
<i>Grasslands and tall forb habitats (E)</i>			
Sub-atlantic semi-dry calcareous grassland	E1.26	Increased mineralization, nitrification and N leaching	15-25
Non-mediterranean dry acid and neutral closed grassland	E1.7	Increased tall grasses, decreased diversity	10-20
Inland dune grasslands	E1.94, E1.95	Increase in nitrophilous graminoids, decline of typical species	10-20
Low and medium altitude hay meadows	E2.2	Decrease in lichens, increase in biomass, increased succession	10-20
Mountain hay meadows	E2.3	Increased tall grasses, decreased diversity	20-30
Moist and wet oligotrophic grasslands	E3.5.1/ E3.5.2	Increase in nitrophilous graminoids, changes in diversity	10-20
Alpine and subalpine grasslands	E4.3 and E4.4	Increase in tall graminoids, decreased diversity, decrease of bryophytes	10-25
Moss and lichen dominated mountain summits	E4.2	Increase in nitrophilous graminoids, changes in diversity	10-15
<i>Heathland habitats (F)</i>			
Northern wet heaths	F4.11	Effects on bryophytes and lichens	5-10
Dry heaths	F4.2	Decreased heather dominance, transition heather to grass, decline in lichens and mosses	10-20
Arctic, alpine and subalpine scrub habitats	F2	Transition heather to grass, decline in lichens	10-20
Dry heaths	F4.2	Decline in lichens, mosses and evergreen shrubs	5-15
<i>Coastal habitat (B)</i>			
Shifting coastal dunes	B1.3	Transition heather to grass, decline in lichens	10-20
Coastal stable dune grasslands	B1.4	Increase in biomass, increased N leaching	10-20
Coastal dune heaths	B1.5	Increase in tall grasses, decreased prostrate plants, increased N leaching	10-20
Moist to wet dune slacks	B1.8	Increase in plant production, increased N leaching, accelerated succession	10-20
<i>Mire, bog and fen habitats (D)</i>			
Raised and blanket bogs	D1	Increase in biomass and tall graminoids	10-25
Poor fens	D2.2 ^d	Changed species composition, N saturation of <i>Sphagnum</i>	5-10
Rich fens	D4.1 ^e	Increase sedges and vascular plant, negative effects on peat mosses	10-20
Mountain rich fens	D4.2	Increase in tall graminoids, decreased diversity, decrease of characteristic mosses	15-35
Empirical data are taken from Achemann and Bobbink (2003).			

3. Exceedance Calculations

In this chapter the calculation of exceedances, i.e., the comparison of critical load with depositions, is described. Most of the material presented here is taken from Posch et al. (1997, 1999); see also Chapter 7 of the Mapping Manual.

3.1 Basic Definitions

Critical loads and levels are derived to characterise the vulnerability of ecosystem (parts, components) in terms of a deposition or concentration. If the critical load of pollutant X at a given location is smaller than the deposition of X at that location, it is said that the critical load is exceeded and the difference is called *exceedance*. In mathematical terms, the exceedance Ex of the critical load $CL(X)$ is given as:

$$(3.1) \quad Ex(X_{dep}) = X_{dep} - CL(X)$$

where X_{dep} is the deposition of pollutant X. In the case of the critical level, the comparison is with the respective concentration quantity. If the critical load is greater than or equal to the deposition, one says that it is not exceeded or there is non-exceedance of the critical load.

An exceedance defined by eq.3.1 can obtain positive, negative or zero value. Since it is in most cases sufficient to know that there is non-exceedance, without being interested in the magnitude of non-exceedance, the exceedance can be also defined as:

$$(3.2) \quad Ex(X_{dep}) = \max\{0, X_{dep} - CL(X)\} = \begin{cases} X_{dep} - CL(X) & X_{dep} > CL(X) \\ 0 & X_{dep} \leq CL(X) \end{cases}$$

An example of the application of this basic equation is the exceedance of the critical load of nutrient N (see section 2.1), which is given by:

$$(3.3) \quad Ex_{nut}(N_{dep}) = N_{dep} - CL_{nut}(N)$$

It should be noted that exceedances differ fundamentally from critical loads, as they are time-dependent. One can speak of *the* critical load of X for an ecosystem, but not of *the* exceedance of it. For exceedances the time for which they have been calculated has to be reported, since – especially in integrated assessment – it is exceedances due to (past or future) *anthropogenic* depositions that are of interest.

Of course, the time-invariance of critical loads and levels has its limitations, certainly when considering a geological time frame. But also during shorter time periods, such as decades or centuries, one can anticipate changes in the magnitude of critical loads due to global (climate) change, which influences the processes from which critical loads are derived. An example of a study of the (first-order) influence of temperature and precipitation changes on critical loads of acidity and nutrient N in Europe can be found in Posch (2002).

The exceedance of a critical load is often misinterpreted as the amount of excess leaching, i.e., the amount leached above the critical/acceptable leaching. This is in general *not* the case as exemplified by the exceedance of the critical load of nutrient N. The excess leaching due to the deposition N_{dep} , Ex_{le} , is given as:

$$(3.4) \quad Ex_{le}(N_{dep}) = N_{le} - N_{le,acc}$$

Inserting the mass balance of N and the deposition-dependent denitrification one obtains for the excess leaching (eqs.2.2–2.5):

$$(3.5) \quad Ex_{le}(N_{dep}) = (1 - f_{de}) \cdot (N_{dep} - CL_{nut}(N)) = (1 - f_{de}) \cdot Ex_{nut}(N_{dep})$$

which shows that a deposition reduction of 1 eq/ha/a reduces the leaching of N by only $1-f_{de}$ eq/ha/a. Only in the simplest case, in which all terms of the mass balances are independent of depositions, does the change in leaching equal the change in deposition.

3.2 Two Pollutants

As shown in Chapter 2, there is no unique critical load of S and N acidity, and all deposition pairs (N_{dep}, S_{dep}) lying on the critical load function lead to the critical leaching of ANC (see eq.2.19 and Figure 2-1). Similarly, there is no unique exceedance of acidity critical loads; although non-exceedance is easily defined (as long as its amount is not important). This is illustrated in Figure 3-2a: Let the point E denote the (current) deposition of N and S. By reducing N_{dep} substantially, one reaches the point Z1 and thus non-exceedance without reducing S_{dep} ; on the other hand one can reach non-exceedance by only reducing S_{dep} (by a smaller amount) until reaching Z3; finally, with a reduction of both N_{dep} and S_{dep} , one can reach non-exceedance as well (e.g. point Z2).

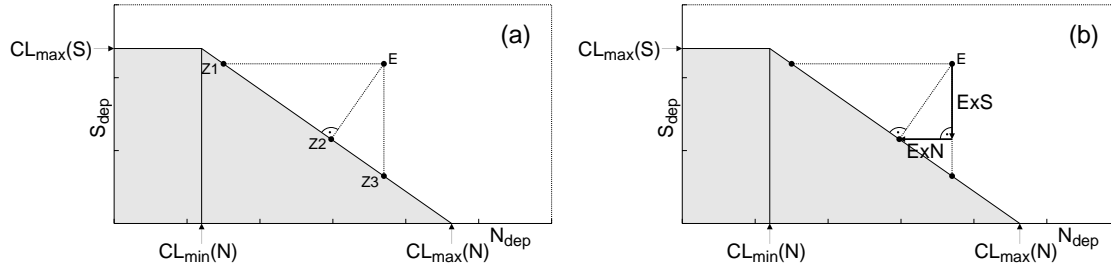


Figure 3-2: Critical load function for S and acidifying N (thick line). The grey-shaded area below the critical load function defines deposition pairs (N_{dep}, S_{dep}) for which there is non-exceedance. (a) The points E and Z1–Z3 show that there is no unique exceedance; (b) the quantities involved in the *definition* of an exceedance (see text for further explanations).

Intuitively, the reduction required in N and S deposition to reach point Z2 (see Figure 3-2b), i.e., the shortest distance to the critical load function, seems a good measure for exceedance. Thus we *define* the exceedance for a given pair of depositions (N_{dep}, S_{dep}) as the sum of the N and S deposition reductions required to reach the critical load function by the ‘shortest’ path. Figure 3-3 depicts the five cases that can arise:

- (a) the deposition falls on or below the critical load function (Region 0). In this case the exceedance is defined as zero (non-exceedance);
- (b) the deposition falls into Region 1 (e.g. point E1). In this case the line perpendicular to the critical load function would yield a negative S_{dep} , and thus every exceedance in this region is defined as the sum of N and S deposition reduction needed to reach point Z1;
- (c) the deposition falls into Region 2 (e.g. point E2): this is the ‘regular’ case, the exceedance is given by the sum of N and S deposition reduction, $ExN+ExS$, required to reach the point Z2, such that the line E2-Z2 is perpendicular to the critical load function;
- (d) Region 3: every exceedance is defined as the sum of N and S deposition reduction needed to reach point Z3;
- (e) Region 4: the exceedance is simply defined as $S_{dep}-CL_{max}(S)$.

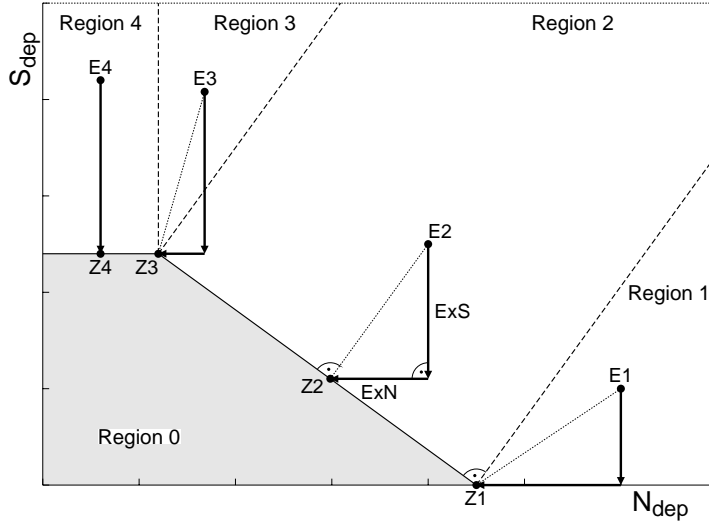


Figure 3-3: Illustration of the different cases for calculating the exceedance for a given critical load function.

The exceedance function can be described by the following equation; note the point Z2 on the critical load function obtained by drawing a perpendicular line through a point in Region 2 (see Figure 3-3) is denoted by (N_0, S_0) :

$$(3.6) \quad Ex(N_{dep}, S_{dep}) = \begin{cases} 0 & \text{if } (N_{dep}, S_{dep}) \in \text{Region 0} \\ N_{dep} - CL_{max}(N) + S_{dep} & \text{if } (N_{dep}, S_{dep}) \in \text{Region 1} \\ N_{dep} - N_0 + S_{dep} - S_0 & \text{if } (N_{dep}, S_{dep}) \in \text{Region 2} \\ N_{dep} - CL_{min}(N) + S_{dep} - CL_{max}(S) & \text{if } (N_{dep}, S_{dep}) \in \text{Region 3} \\ S_{dep} - CL_{max}(S) & \text{if } (N_{dep}, S_{dep}) \in \text{Region 4} \end{cases}$$

The function thus defined fulfils the criteria of a meaningful exceedance function: it is zero, if there is no exceedance of critical loads, positive when there is exceedance, and increasing in value when the point (N_{dep}, S_{dep}) moves away from the critical load function.

The computation of the exceedance function requires the estimation of the coordinates of the point Z2 on the critical load function. If (x_1, y_1) and (x_2, y_2) are two arbitrary points of a straight line g and (x_e, y_e) another point (not on that line), then the coordinates (x_0, y_0) of the point obtained by intersecting the line passing through (x_e, y_e) and perpendicular to g (called the ‘foot’ or ‘foot of the perpendicular’) are given by:

$$(3.7a) \quad x_0 = (d_1 s + d_2 v) / d^2 \quad \text{and} \quad y_0 = (d_2 s - d_1 v) / d^2$$

with

$$(3.7b) \quad d_1 = x_2 - x_1, \quad d_2 = y_2 - y_1, \quad d^2 = d_1^2 + d_2^2$$

and

$$(3.7c) \quad s = x_e d_1 + y_e d_2, \quad v = x_1 d_2 - y_1 d_1 = x_1 y_2 - y_1 x_2$$

Applying these equations to $(x_1, y_1) = (CL_{min}(N), CL_{max}(S))$, $(x_2, y_2) = (CL_{max}(N), 0)$ and $(x_e, y_e) = (N_{dep}, S_{dep})$ one obtains the point $(x_0, y_0) = (N_0, S_0)$ (Z2 in Figure 3-3). Finally, one has to determine into which of the regions (Region 0 through Region 4 in Figure 3-3) a given pair of deposition (N_{dep}, S_{dep}) falls.

3.3 Target Loads

In the previous sections the excess of depositions over critical loads has been defined as exceedance. In the case of target loads or target load functions the same quantities as defined above can be calculated, but if they are positive, we talk about the *non-achievement* of the target load; if it is zero or negative, we say the target (load) for a given year has been achieved.

4. Dynamic Modelling

Dynamic modelling is the logical extension of critical loads. Critical loads are based on a steady-state concept, they are the constant depositions an ecosystem can tolerate in the long run, i.e., after it has equilibrated with these depositions. However, many ecosystems are not in equilibrium with present or projected depositions, since there are processes ('buffer mechanisms') at work, which delay the reaching of an equilibrium (steady state) for years, decades or even centuries. By definition, critical loads do not provide any information on these time scales. Dynamic models are needed to assess time delays of recovery in regions where critical loads cease being exceeded and time delays of damage in regions where critical loads continue to be exceeded.

Here we explain the use (and constraints) of dynamic modelling in support of the effects-oriented work under the LRTAP Convention. For the sake of simplicity and in order to avoid the somewhat vague term 'ecosystem', we refer in the sequel to non-calcareous (forest) soils. However, most of the considerations hold for surface water systems as well, since their water quality is strongly influenced by properties of and processes in catchment soils. A summary for the dynamic modelling of surface waters can be found in Jenkins et al. (2003).

4.1 Why dynamic modelling?

In the causal chain from deposition of strong acids to damage to key indicator organisms there are two major links that can give rise to delays. Biogeochemical processes can delay the chemical response in soil, and biological processes can further delay the response of indicator organisms, such as damage to trees in forest ecosystems. The static models to determine critical loads consider only the steady-state condition, in which the chemical and biological response to a (new) (constant) deposition is complete. Dynamic models, on the other hand, attempt to estimate the time required for a new (steady) state to be achieved.

With critical loads, i.e. in the steady-state situation, only two cases can be distinguished when comparing them to deposition: (1) the deposition is below critical load(s), i.e. does not exceed critical loads, and (2) the deposition is greater than critical load(s), i.e. there is critical load exceedance. In the first case there is no (apparent) problem, i.e. no reduction in deposition is deemed necessary. In the second case there is, by definition, an increased risk of damage to the ecosystem. Thus a critical load serves as a warning as long as there is exceedance, since it states that deposition should be reduced. However, it is often assumed that reducing deposition to (or below) critical loads immediately removes the risk of 'harmful effects', i.e. the chemical criterion (e.g. the Al/Bc-ratio¹) that links the critical load to the (biological) effect(s), immediately attains a non-critical ('safe') value, and that there is immediate

¹ In Chapter 5 (and elsewhere) the Bc/Al-ratio is used. However, this ratio becomes infinite when the Al concentration approaches zero. To avoid this inconvenience, its inverse, the Al/Bc-ratio, is used here.

biological recovery as well. But the reaction of soils, especially their solid phase, to changes in deposition is delayed by (finite) buffers, the most important being the cation exchange capacity (CEC). These buffer mechanisms can delay the attainment of a critical chemical parameter, and it might take decades or even centuries, before equilibrium (steady state) is reached. These finite buffers are not included in the critical load formulation, since they do not influence the steady state, but only the time to reach it. Therefore, dynamic models are needed to estimate the times involved in attaining a certain chemical state in response to deposition scenarios, e.g. the consequences of ‘gap closures’ in emission reduction negotiations. In addition to the delay in chemical recovery, there is likely to be a further delay before the ‘original’ biological state is reached, i.e. even if the chemical criterion is met (e.g. $A/B_c < 1$), it will take time before biological recovery is achieved.

Figure 4-1 summarises the possible development of a (soil) chemical and biological variable in response to a ‘typical’ temporal deposition pattern. Five stages can be distinguished:

Stage 1: Deposition was and is below the critical load (CL) and the chemical and biological variables do not violate their respective criteria. As long as deposition stays below the CL, this is the ‘ideal’ situation.

Stage 2: Deposition is above the CL, but (chemical and) biological criteria are not violated because there is a time delay before this happens. No damage is likely to occur at this stage, therefore, despite exceedance of the CL. The time between the first exceedance of the CL and the first violation of the biological criterion (the first occurrence of actual damage) is termed the *Damage Delay Time* ($DDT = t_3 - t_1$).

Stage 3: The deposition is above the CL and both the chemical and biological criteria are violated. Measures (emission reductions) have to be taken to avoid a (further) deterioration of the ecosystem status.

Stage 4: Deposition is below the CL, but the (chemical and) biological criteria are still violated and thus recovery has not yet occurred. The time between the first non-exceedance of the CL and the subsequent non-violation of both criteria is termed the *Recovery Delay Time* ($RDT = t_6 - t_4$).

Stage 5: Deposition is below the CL and both criteria are no longer violated. This stage is similar to Stage 1 and only at this stage can the ecosystem be considered to have recovered.

Stages 2 and 4 can be subdivided into two sub-stages each: Chemical delay times ($DDT_c = t_2 - t_1$ and $RDT_c = t_5 - t_4$; dark grey in Figure 6-1) and (additional) biological delay times ($DDT_b = t_3 - t_2$ and $RDT_b = t_6 - t_5$; light grey). Very often, due to the lack of operational biological response models, damage and recovery delay times mostly refer to chemical recovery alone and this is used as a surrogate for overall recovery. It is also important to note that recovery does not follow the same, (inverse) path of damage, since there is a so-called hysteresis in these natural systems (see, e.g., Warfvinge et al. 1992b).

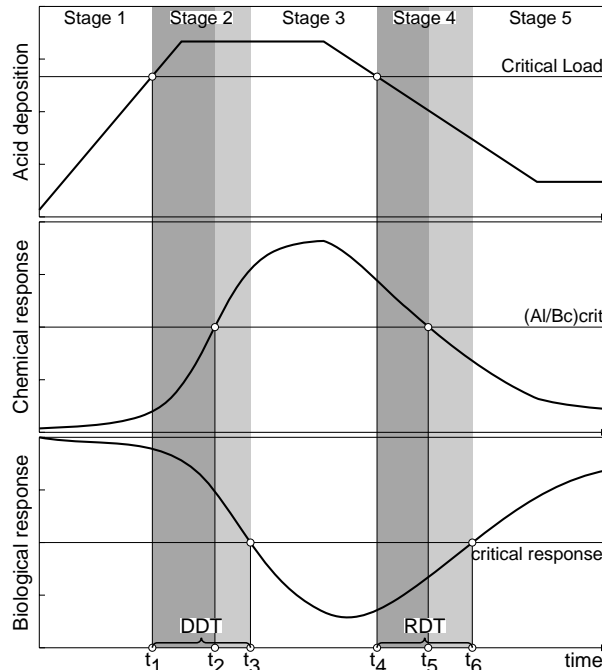


Figure 4-1: ‘Typical’ past and future development of the acid deposition effects on a soil chemical variable (Al/Bc-ratio) and the corresponding biological response in comparison to the critical values of those variables and the critical load derived from them. The delay between the (non)exceedance of the critical load, the (non)violation of the critical chemical criterion and the crossing of the critical biological response is indicated in grey shades, highlighting the Damage Delay Time (DDT) and the Recovery Delay Time (RDT) of the system.

4.2 Compatibility of critical loads and dynamic modelling

Steady-state models (critical loads) have been used to negotiate emission reductions in Europe. In this context, an emission reduction is judged successful if non-exceedance of critical loads is attained. To gain insight into the time delay between the attainment of non-exceedance and actual chemical (and biological) recovery, dynamic models are needed. Thus if dynamic models are to be used to assess recovery with respect to negotiated targets under the LRTAP Convention they should be compatible with the steady-state models used for calculating critical loads. In other words, when critical loads are used as input to the dynamic model, the (chemical) parameter chosen as the criterion in the critical load calculation has to attain the critical value (after the dynamic simulation has reached steady state). But this also means that concepts and equations used in the dynamic model should be an extension of the concepts and equations employed in deriving the steady-state model. For example, if critical loads are calculated with the Simple Mass Balance (SMB) model (see Chapter 2), this model should be the steady-state version of the dynamic model used (e.g., the VSD model, Posch and Reinds 2008).

Due to a lack of (additional) data, it may be impossible to run dynamic models on all sites in a country for which critical loads have been calculated. The selection of the subset of sites, at which dynamic models are applied, has to be representative enough to allow comparison with results obtained with critical loads.

4.3 Models

Descriptions of models can be found in the 'Dynamic Modelling Manual' (Posch et al. 2003b), and in abridged form, in Chapter 6 of the Mapping Manual (UBA 2004). Especially for the VSD model see also Posch and Reinds (2008).

References

- Achermann B, Bobbink R (eds.), 2003, Empirical critical loads for nitrogen: Expert workshop, Berne 11-13 November 2003, Environmental documentatuiou 164, Swiss Agency for the Environment, forests and landscape.
- Berendse F, Beltman B, Bobbink R, Kwant M, Schmitz MB, 1987. Primary production and nutrient availability in wet heathland ecosystems. *Acta Oec./Oecol. Plant.* 8: 265-276
- Bobbink R, Hornung M, Roelofs JGM, 1998. The effects of air-borne pollutants on species diversity in natural and semi-natural European vegetation. *Journal of Ecology* 86: 717-738
- Breeuwisma A, Chardon JP, Kragt JF, De Vries W, 1991. Pedotransfer functions for denitrification. Final Report of the project 'Nitrate in Soils', DG XII, European Community, Brussels, pp 207-215
- Burman R, Pochop LO, 1994. *Evaporation, Evapotranspiration and Climatic Data*. Developments in Atmospheric Science 22, Elsevier, Amsterdam, 278 pp
- Cronan CS, Walker WJ, Bloom PR, 1986. Predicting aqueous aluminium concentrations in natural waters. *Nature* 324: 140-143
- De Vries W, 1988. Critical deposition levels for nitrogen and sulphur on Dutch forest ecosystems. *Water, Air and Soil Pollution* 42: 221-239
- De Vries W, Hol A, Tjalma S, Voogd JC, 1990. Literature study on the amounts and residence times of elements in forest ecosystems (in Dutch). Rapport 94, DLO Winand Staring Centre, Wageningen, The Netherlands, 205 pp
- De Vries W, 1991. Methodologies for the assessment and mapping of critical loads and of the impact of abatement strategies on forest soils. Report 46, DLO Winand Staring Centre, Wageningen, The Netherlands, 109 pp
- De Vries W, Posch M, Reinds GJ, Kämäri J, 1993. Critical loads and their exceedance on forest soils in Europe. Report 58 (revised version), DLO Winand Staring Centre, Wageningen, The Netherlands, 116 pp
- De Vries W, 1994. Soil response to acid deposition at different regional scales. PhD thesis, Agricultural University Wageningen, Wageningen, The Netherlands, 487 pp
- De Vries W, Reinds GJ, Posch M, 1994. Assessment of critical loads and their exceedances on European forests using a one-layer steady-state model. *Water, Air and Soil Pollution* 72: 357-394
- De Vries W, Posch M, 2003. Derivation of cation exchange constants for sand loess, clay and peat soils on the basis of field measurements in the Netherlands. Alterra-Rapport 701, Alterra Green World Research, Wageningen, The Netherlands, 50 pp
- De Vries W, Reinds GJ, Posch M, Sanz MJ, Krause GHM, Calatayud V, Renaud JP, Dupouey JL, Sterba H, Vel EM, Dobbertin M, Gundersen P, Voogd JCH, 2003. Intensive Monitoring of Forest Ecosystems in Europe. Technical Report 2003, EC-UNECE, Brussels and Geneva, 161 pp
- De Vries W, Kros H, Reinds GJ, Wamelink W, Mol J, Van Dobben H, Bobbink R, Emmett B, Smart S, Evans C, Schlutow A, Kraft P, Belyazid S, Sverdrup H, Van Hinsberg A, Posch M, Hettelingh J-P (2007) Development in deriving critical limits and modelling critical loads of nitrogen for terrestrial ecosystems in Europe, Alterra-MNP/CCE report, Alterra report 1382.
- Driscoll CT, Lehtinen MD, Sullivan TJ, 1994. Modeling the acid-base chemistry of organic solutes in Adirondack, New York, lakes. *Water Resources Research* 30: 297-306
- Dutch J, Ineson P, 1990. Denitrification of an upland forest site. *Forestry* 63: 363-377
- Eurosoil, 1999. Metadata: Soil Geographical Data Base of Europe v.3.2.8.0. Joint Research Centre, Ispra, Italy.
- FAO, 1981. FAO-Unesco Soil Map of the World, 1:5.000.000; Volume V Europe, Unesco-Paris, 199 pp
- Galloway J, Townsend AR, Erisman JW, Bekunda M, Cai Zucong, Freney JR, Martinelli LA, Seitzinger SP, Sutton MA (2008) Transformation of the nitrogen cycle: Recent trends, questions and potential solutions, *Science* 320:889-892.
- Hall J, Ashmore M, Curtis C, Doherty C, Langan S, Skeffington R, 2001. UN/ECE expert workshop: Chemical criteria and critical limits. In: Posch et al. (2001) *op. cit.*, pp. 67-71
- Henriksen A, Posch M, 2001. Steady-state models for calculating critical loads of acidity for surface waters. *Water, Air and Soil Pollution: Focus* 1: 375-398
- Hettelingh J-P, Posch M, De Smet PAM, Downing RJ (1995) The use of critical loads in emission reduction agreements in Europe, *Water, Air an Soil Pollution* 85:2381-2389
- Hettelingh J-P, Posch M, De Smet PAM (2001) Multi-effect critical loads used in multi-pollutant reduction agreements in Europe. *Water, Air and Soil Pollution* 130: 1133-1138.

- Hettelingh J-P, Posch M, Slootweg J, Reinds GJ, Spranger T, Tarrason L (2007) Critical loads and dynamic modelling to assess European areas at risk of acidification and eutrophication. *Water, Air and Soil Pollution: Focus* 7:379-384
- Hornung M, Sutton MA, Wilson RB (eds), 1995. Mapping and Modelling of Critical Loads for Nitrogen: A Workshop Report. Proceedings of the Grange-over-Sands Workshop 24-26 October 1994. Institute for Terrestrial Ecology, United Kingdom, 207 pp
- Jacobsen C, Rademacher P, Meesenburg H, Meiwes KJ, 2002. Element contents in tree compartments – Literature study and data collection (in German). Report, Niedersächsische Forstliche Versuchsanstalt, Göttingen, Germany, 80 pp
- Jenkins A, Cosby BJ, Ferrier RC, Larssen T, Posch M, 2003. Assessing emission reduction targets with dynamic models: deriving target load functions for use in integrated assessment. *Hydrology and Earth System Sciences* 7(4): 609-617
- Johansson M, Tarvainen T, 1997. Estimation of weathering rates for critical load calculations in Finland. *Environmental Geology* 29(3/4): 158-164
- Johnson DW, Cole DW, Gessel SP, 1979. Acid precipitation and soil sulfate adsorption properties in a tropical and in a temperate forest soil. *Biotropica* 11: 38-42
- Johnson DW, Henderson GS, Huff DD, Lindberg SE, Richter DD, Shriner DS, Todd DE, Turner J, 1982. Cycling of organic and inorganic sulphur in a chestnut oak forest. *Oecologia* 54: 141-148
- Johnson DW, 1984. Sulfur cycling in forests. *Biogeochemistry* 1: 29-43
- Joki-Heiskala P, Johansson M, Holmberg M, Mattson T, Forsius M, Kortelainen P, Hallin L, 2003. Long-term base cation balances of forest mineral soils in Finland. *Water, Air and Soil Pollution* 150: 255-273
- Kimmins JP, Binkley D, Chatarpaul L, De Catanzaro J, 1985. Biogeochemistry of temperate forest ecosystems: Literature on inventories and dynamics of biomass and nutrients. Information Report PI-X-47E/F, Petawawa National Forestry Institute, Canada, 227 pp
- Monteith JL, Unsworth M, 1990. *Principles of Environmental Physics* (2nd edition). Arnold, London, 291 pp.
- Mulder J, Stein A, 1994. The solubility of aluminum in acidic forest soils: long-term changes due to acid deposition. *Geochimica et Cosmochimica Acta* 58: 85-94
- NEG/ECP, 2001. Protocol for Assessment and Mapping of Forest Sensitivity to Atmospheric S and N Deposition, prepared by the NEG/ECP Forest Mapping Group, New England Governors/Eastern Canadian Premiers, 'Acid Rain Action Plan 2001, Action Item 4: Forest Mapping Research Project', 79 pp
- Nilsson J, Grennfelt P (eds), 1988. Critical Loads for Sulphur and Nitrogen. Environmental Report 1988:15 (NORD 1988:97), Nordic Council of Ministers, Copenhagen, 418 pp
- Oliver BG, Thurman EM, Malcolm RL, 1983. The contribution of humic substances to the acidity of colored natural waters. *Geochimica et Cosmochimica Acta* 47: 2031-2035
- Olsson M, Rosén K, Melekrud P-A, 1993. Regional modelling of base cation losses from Swedish forest soils due to whole-tree harvesting. *Applied Geochemistry*, Suppl. Issue No.2, pp. 189-194
- Paces T, 1983. Rate constants of dissolution derived from the measurements of mass balance in hydrological catchments. *Geochimica et Cosmochimica Acta* 47: 1855-1863
- Posch M, Hettelingh J-P, Sverdrup HU, Bull K, De Vries W, 1993. Guidelines for the computation and mapping of critical loads and exceedances of sulphur and nitrogen in Europe. In: RJ Downing, J-P Hettelingh, PAM de Smet (eds) Calculation and Mapping of Critical Loads in Europe. CCE Status Report 1993, RIVM Report 259101003, Bilthoven, The Netherlands, pp. 25-38 www.mnp.nl/cce
- Posch M, De Smet PAM, Hettelingh J-P, Downing RJ (eds), 1995. Calculation and mapping of critical thresholds in Europe. Status Report 1995, Coordination Centre for Effects, RIVM Report 259101004, Bilthoven, Netherlands, iv+198 pp www.mnp.nl/cce
- Posch M, Hettelingh J-P, De Smet PAM, Downing RJ (eds), 1997. Calculation and mapping of critical thresholds in Europe. Status Report 1997, Coordination Centre for Effects, RIVM Report 259101007, Bilthoven, Netherlands, iv+163 pp www.mnp.nl/cce
- Posch M, De Smet PAM, Hettelingh J-P, Downing RJ (eds), 1999. Calculation and mapping of critical thresholds in Europe. Status Report 1999, Coordination Centre for Effects, RIVM Report 259101009, Bilthoven, Netherlands, iv+165 pp www.mnp.nl/cce
- Posch M, 2000. Critical loads of acidity: Possible modifications. In: M Holmberg (ed) Critical Loads Calculations: Developments and Tentative Applications. TemaNord 2000:566, Nordic Council of Ministers, Copenhagen, pp.8-19
- Posch M, De Smet PAM, Hettelingh J-P, Downing RJ (eds), 2001. Modelling and Mapping of Critical Thresholds in Europe. CCE Status Report 2001, RIVM Report 259101010, Bilthoven, Netherlands, iv+188 pp www.mnp.nl/cce
- Posch M, 2002. Impacts of climate change on critical loads and their exceedances in Europe. *Environmental Science and Policy* 5(4): 307-317
- Posch M, Hettelingh J-P, Slootweg J, Downing RJ (eds), 2003. Modelling and Mapping of Critical Thresholds in

- Europe. CCE Status Report 2003, RIVM Report 259101013, Bilthoven, The Netherlands, 132 pp
www.mnp.nl/cce
- Posch M, Hettelingh J-P, Slootweg J (eds), 2003b. Manual for dynamic modelling of soil response to atmospheric deposition. RIVM Report 259101012, Bilthoven, The Netherlands, 69 pp www.mnp.nl/cce
- Posch M, Eggenberger U, Kurz D, Rihm B, 2007. Critical loads of acidity for alpine lakes. A weathering rate calculation model and the generalized First-order Acidity Balance (FAB) model applied to alpine lake catchments. Environmental Studies 0709, Federal Office for the Environment, Berne, Switzerland, 69 pp
www.environment-switzerland.ch/uw-0709-e
- Reinds GJ, Posch M, De Vries W, 2001. A semi-empirical dynamic soil acidification model for use in spatially explicit integrated assessment models for Europe. Alterra Report 084, Alterra Green World Research, Wageningen, The Netherlands, 55 pp
- Posch M, Reinds GJ, 2008. VSD – A Very Simple Dynamic soil acidification model for scenario analyses and target load calculations. *Environmental Modelling & Software* (forthcoming)
- Reuss JO, 1983. Implications of the calcium-aluminum exchange system for the effect of acid precipitation on soils. *Journal of Environmental Quality* 12(4): 591-595
- Reuss JO, Johnson DW, 1986. *Acid Deposition and the Acidification of Soils and Waters*. Ecological Studies 59, Springer, New York, 119 pp
- Rosén K, 1990. The critical load of nitrogen to Swedish forest ecosystems. Department of Forest Soils, Swedish University of Agricultural Sciences, Uppsala, Sweden, 15 pp
- Rosén K, Gundersen P, Tegnhammar L, Johansson M, Frogner T, 1992. Nitrogen enrichment in Nordic forest ecosystems – The concept of critical loads. *Ambio* 21: 364-368
- Santore RC, Driscoll CT, Aloï M, 1995. A model of soil organic matter and its function in temperate forest soil development. In: WW McFee, JM Kelly (eds) *Carbon Forms and Functions in Forest Soils*. Soil Science Society of America, Madison, Wisconsin, pp.275-298
- Slootweg J, Posch M, Hettelingh JP (2007) Critical Loads of Nitrogen and dynamic Modelling, CCE Progress Report 2007, MNP Report 500090001/2007, www.mnp.nl/cce
- Sogn TA, Stuanes AO, Abrahamsen G, 1999, The capacity of forest soil to absorb anthropogenic N. *Ambio* 28: 346-349
- Steenworden J, 1984. Influence of changes in water management on water quality (in Dutch). Report 1554, Institute for Land and Water Management, Wageningen, The Netherlands
- Sverdrup HU, 1990. *The Kinetics of Base Cation Release due to Chemical Weathering*. Lund University Press, Lund, Sweden, 246 pp
- Sverdrup H, De Vries W, Henriksen A, 1990. Mapping Critical Loads. Environmental Report 1990:14 (NORD 1990:98), Nordic Council of Ministers, Copenhagen, 124 pp
- Sverdrup H, Ineson P, 1993. Kinetics of denitrification in forest soils. Compuscript, 18 pp
- Sverdrup H, Warfvinge P, 1993. The effect of soil acidification on the growth of trees, grass and herbs as expressed by the (Ca+Mg+K)/Al ratio. Reports in Ecology and Environmental Engineering 2, Lund University, Lund, Sweden, 177 pp
- Sverdrup H, De Vries W, 1994. Calculating critical loads for acidity with the simple mass balance method. *Water, Air and Soil Pollution* 72: 143-162
- Tipping E, 1994. WHAM – A chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. *Computers & Geosciences* 20(6): 973-1023
- UBA, 2004. Manual on methodologies and criteria for modelling and mapping critical loads & levels and air pollution effects, risks and trends. Texte 52/04, Umweltbundesamt, Berlin www.icpmapping.org
- Ulrich B, Sumner ME (eds), 1991. *Soil Acidity*. Springer, Berlin, 224 pp
- UNECE, 1995. Calculation of critical loads of nitrogen as a nutrient. Summary report on the development of a library of default values. Document EB.AIR/WG.1/R.108, United Nations Economic Commission for Europe, Geneva, 7 pp
- UNECE, 2001. Workshop on chemical criteria and critical limits. Document EB.AIR/WG.1/2001/13, United Nations Economic Commission for Europe, Geneva, 8 pp
- Van Dam D, 1990 Atmospheric deposition and nutrient cycling in chalk grassland. PhD Thesis, University of Utrecht, Utrecht, The Netherlands, 119 pp
- Van der Salm C, 1998. Assessment of weathering rates in Dutch loess and clay soils at pH 3.5, using laboratory experiments. *Geoderma* 85: 41-62
- Van der Salm C, De Vries W, 2001. A review of the calculation procedure for critical acid loads for terrestrial ecosystems. *The Science of the Total Environment* 271: 11-25
- Van Miegroet H, Cole DW, 1984. The impact of nitrification on soil acidification and cation leaching in a red alder ecosystem. *Journal of Environmental Quality* 13: 586-590
- Warfvinge P, Sverdrup H, 1992. Calculating critical loads of acid deposition with PROFILE - A steady-state soil

- chemistry model. *Water, Air and Soil Pollution* 63: 119-143 www2.chemeng.lth.se
- Warfvinge P, Sverdrup H, Rosén K, 1992. Calculating critical loads for N to forest soils. In: P Grennfelt, E Thörmelöf (eds) *Critical Loads for Nitrogen*, Nord 1992:41, Nordic Council of Ministers, Copenhagen, Denmark, pp. 405-417
- Warfvinge P, Holmberg M, Posch M, Wright RF, 1992b. The use of dynamic models to set target loads. *Ambio* 21: 369-376
- Warfvinge P, Sverdrup H, 1995. Critical loads of acidity to Swedish forest soils. *Reports in Ecology and Environmental Engineering* 5, Lund University, Lund, Sweden, 104 pp