5.3 Modelling Critical Loads for Terrestrial Ecosystems

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

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

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

Since the SMB model describes steady-state conditions, it requires long-term averages for input fluxes. Short-term variations – e.g., episodic, seasonal, 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. at least one rotation period for forests. Ecosystem interactions and processes like competition, pests, herbivore influences etc. are not considered in the SMB model. Although the SMB model is formulated for undisturbed (semi-natural) ecosystems, the effects of extensive management, such as grazing and the burning of moor, could be included.

Besides the single-layer SMB model, there exist multi-layer steady-state models for calculating critical loads. Examples are the MACAL model (De Vries 1988) and the widely-used PROFILE model (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 reader is referred to the literature.

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

5.3.1 Critical loads of nutrient nitrogen (eutrophication)

5.3.1.1 Model derivation

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

(5.1)

$$N_{dep} + N_{fix} = N_{ad} + N_i + N_u + N_{de} + N_{eros} + N_{fire} + N_{vol} + N_{le}$$

where:

N_{dep} = total N deposition

N_{fix} = N 'input' by biological fixation

N_{ad} = N adsorption

N_i = long-term net immobilisation of N in soil organic matter

N_u = net removal of N in harvested vegetation and animals

N_{de} = flux of N to the atmosphere due to denitrification

N_{eros} = N losses through erosion

N_{fire} = N losses in smoke due to (wild or controlled) fires

N_{vol} = N losses to the atmosphere via NH_3 volatilisation

N_{le} = leaching of N below the root zone

The units used are $eq/ha/yr$ (or $mol_c/ha/yr$ in proper SI nomenclature).

The following assumptions lead to a simplification of eq. 5.1:

- Nitrogen adsorption, e.g., the adsorption of NH_4 by clay minerals, can temporarily lead to an accumulation of N in the soil, however it is stored/released only when the deposition *changes*, and can thus be neglected in steady state considerations.
- Nitrogen fixation is negligible in most (forest) ecosystems, except for N-fixing species.
- The loss of N due to fire, erosion and volatilisation is small for most ecosystems in Europe, and therefore neglected in the following discussion. Alternatively, one could replace N_i by $N_i+N_{eros}+N_{fire}+N_{vol}-N_{fix}$ in the subsequent equations.
- The leaching of ammonium (NH_4) can be neglected in all forest ecosystems due to (preferential) uptake and complete nitrification within the root zone (i.e. $NH_{4,le}=0$, $N_{le}=NO_{3,le}$).

Under these simplifying assumptions eq. 5.1 becomes:

(5.2)

$$N_{dep} = N_i + N_u + N_{de} + N_{le}$$

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. 5.2, the deposition of N becomes the critical load of nutrient nitrogen, $CL_{nut}(N)$:

(5.3)

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

In deriving the critical load of nutrient N as eq. 5.3, 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. 5.2 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):

(5.4)

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

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. 5.2 and solving for the deposition leads to the following expression for the critical load of nutrient N:

(5.5)

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

An alternative, non-linear, equation for the deposition-dependence of denitrification has been proposed by Sverdrup and Ineson (1993) based on the Michaelis-Menten reaction mechanism and includes a dependence on soil moisture, pH and temperature. Also in this case $CL_{nut}(N)$ 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. 5.3 or eq. 5.5, the N fluxes should be estimated as long-term averages derived from conditions not influenced by elevated anthropogenic N inputs.

5.3.1.2 The acceptable leaching of nitrogen

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

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

where $[N]_{acc}$ is the acceptable N concentration (eq/m^3) and Q is the precipitation surplus (in $m^3/ha/yr$). Values for acceptable N concentrations are given in Table 5.7.

To convert the values in Table 5.7 to eq/m^3 divide them by 14. In general, the low leaching values from the above table lead to critical loads that are lower than empirical data on vegetation changes (e.g. Bobbink et al. 1998). It is the increase in N availability through enhanced N cycling that triggers changes (Berendse et al. 1987).

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.

Table 5.7: Critical (acceptable) N concentrations in soil solution for calculating CLnut(N)
updated 12.07.2007, see next page

Impact	$[N]_{acc}$ **(mgN/L = gN/m^3)**	$[N]_{acc}$ **(eq/m^3)**

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5.3.1.2 The acceptable leaching of nitrogen

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

$$N_{le(acc)} = Q \cdot [N]_{acc} \tag{5.6}$$

where $[N]_{acc}$ is the acceptable N concentration (eq/m^3) and Q is the precipitation surplus (in m^3/ha/yr). Values for acceptable N concentrations are given in Table 5.7 (see De Vries et al. 2007).

Table 5.7: Critical (acceptable) N concentrations in soil solution for calculating $CL_{nut}(N)$.

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

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

To convert the values in Table 5-7 to eq/m^3 divide them by 14. In general, the low leaching values from the above table lead to critical loads that are lower than empirical data on vegetation changes (e.g. Bobbink et al. 1998). It is the increase in N availability through enhanced N cycling that triggers changes (Berendse et al. 1987).

5.3.1.3 Sources and derivation of input data

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

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

Using data from Swedish forest soil plots, Rosén et al. (1992) estimated the annual N immobilisation since the last glaciation at 0.2–0.5 *kgN/ha/yr* (14.286–35714 *eq/ha/yr*). Considering that the immobilisation of N is probably higher in warmer climates, values of up to 1 *kgN/ha/yr* (71.428 *eq/ha/yr*) could be used for N_i, without causing unsustainable accumulation of N in the soil. It should be pointed out, however, that even higher values (closer to present-day immobilisation rates) have been used in critical load calculations. Although studies on the capacity of forests to absorb nitrogen have been carried out (see, e.g., Sogn et al. 1999), there is no consensus yet on long-term sustainable immobilisation rates.

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

(5.7)

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

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

(5.8)

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

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

Values for the density of stem wood of most trees are in the range of 400–500 kg/m³ for conifers and 550–700 kg/m³ for deciduous trees. The branch-to-stem ratio is about 0.15 kg/kg for conifers and 0.20 kg/kg for deciduous trees (Kimmins et al. 1985, De Vries et al. 1990). According to Swedish data (Rosén 1990; see also Reinds et al. 2001) the contents of N in stems are 1 g/kg for conifers and 1.5 g/kg in deciduous trees, whereas in branches of all tree species the N content is 4 g/kg in the south and 2 g/kg in the north. In a recent report Jacobsen et al. (2002) have summarised the results of a large number of studies on that subject, and Table 5.8 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.

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

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 $kgN/ha/yr$, 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 $kgN/ha/yr$ (=7.14–214.3 $eq/ha/yr$), where the higher values apply to wet(ter) soils; rates for well drained soils are generally below 0.5 $kgN/ha/yr$.

With respect to deposition-dependent denitrification, values for the denitrification fraction f_{de} have been given by De Vries et al. (1993) based on data from Breeuwsma et al. (1991) and Steenvorden (1984): f_{de}=0.8 for peat soils, 0.7 for clay soils, 0.5 for sandy soils with gleyic features and f_{de}=0–0.1 for sandy soils without gleyic features. Reinds et al. (2001) related the denitrification fraction to the drainage status of the soil according to Table 5.9:

Precipitation surplus:

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

Table 5.8: Mean (and standard deviation) of the element contents in stems and branches (both incl. bark) of four tree species (Jacobsen et al. 2002; the number of data points ranges from 6 to 32).

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 *quercus spp*	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 *fagus sylv.*	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 *picea abies*	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 *pinus sylv.*	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.

Table 5.9: Denitrification fraction f_{de} as a function of the soil drainage (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

5.3.2 Critical loads of acidity

5.3.2.1 Model derivation: the Simple Mass Balance (SMB) model

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

(5.9)

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

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 $X_{le}=Q\cdot[X]$, where $[X]$ is the soil solution concentration of ion X and Q is the precipitation surplus. All fluxes are expressed in equivalents (moles of charge) per unit area and time $(eq/ha/yr)$. The concentrations of OH and CO_3 are assumed zero, which is a reasonable assumption even for calcareous soils. The leaching of Acid Neutralising Capacity (ANC) is defined as:

(5.10)

$$ANC_{le} = HCO_{3,le} + RCOO_{le} - H_{le} - Al_{le}$$

Combination with eq. 5.9 yields:

(5.11)

$$BC_{le} + NH_{4,le} - SO_{4,le} - NO_{3,le} - Cl_{le} = ANC_{le}$$

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

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

(5.12)

$$Cl_{le} = Cl_{dep}$$

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:

(5.13)

$$BC_{le} = BC_{dep} + BC_w - Bc_u$$

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

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

(5.14)

$$S_{le} = S_{dep} - S_{ad} - S_i - S_u - S_{re} - S_{pr}$$

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 have 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 S 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:

(5.15)

$$SO_{4,le} = S_{dep}$$

For nitrogen, the mass balance in soil is (see Section 5.3.1):

(5.16)

$$\begin{aligned} N_{le} &= N_{dep} + N_{fix} - N_{ad} - N_i - N_u - N_{de} \\ &\quad - N_{eros} - N_{fire} - N_{vol} \end{aligned}$$

where the subscripts fix refers to fixation of N, *de* to denitrification, and $eros$, $fire$ and vol to the loss of N due to erosion, forest fires and volatilisation, respectively. N_i is the long-term immobilisation of N in the root zone, and N_u the net growth uptake (see above). Furthermore, the leaching of NH_4 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. 5.16 simplifies to:

(5.17)

$$N_{le} = NO_{3,le} = N_{dep} - N_i - N_u - N_{de}$$

Inserting eqs. 5.12, 5.13, 5.15 and 5.17 into eq. 5.11 leads to the following simplified charge balance for the soil compartment:

(5.18)

$$\begin{aligned} S_{dep} + N_{dep} &= BC_{dep} - Cl_{dep} + BC_w - Bc_u \\ &\quad + N_i + N_u + N_{de} - ANC_{le} \end{aligned}$$

Strictly speaking, we should replace $NO_{3,le}$ in the charge balance not by the right-hand side of eq. 5.17, 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. 5.18, keeping this constraint in mind.

Since the aim of the LRTAP Convention is to reduce *anthropogenic* emissions of S and N, sea-salt derived sulphate should not be considered in the balance. To retain charge balance, this is achieved by applying a sea-salt correction to sulphate, chloride and base cations, using either Cl or Na as a tracer, whichever can be (safer) assumed to originale from sea-salts only. Denoting sea-salt corrected depositions with an asterisk, 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 Chapter 2.

For given values for the sources and sinks of S, N and Bc, eq. 5.18 allows the calculation of the leaching of ANC, and thus assessment of the acidification status of the soil. Conversely, critical loads of S, $CL(S)$, and N, $CL(N)$, can be computed by defining a critical ANC leaching, $ANC_{le,crit}$:

(5.19)

$$\begin{aligned} CL(S) + CL(N) &= BC^*_{dep} - Cl^*_{dep} + BC_w - Bc_u \\ &\quad + N_i + N_u + N_{de} - ANC_{le,crit} \end{aligned}$$

A so-called critical load of potential acidity has earlier been defined (see Sverdrup et al. 1990) as:

(5.20)

$$\begin{aligned} CL(Ac_{pot}) &= BC_w - Bc_u \\ &\quad + N_i + N_u + N_{de} - ANC_{le,crit} \end{aligned}$$

with $Ac_{pot} = S_{dep}+N_{dep}-BC^*_{dep}+Cl^*_{dep}$. The term 'potential' is used since NH_3 is treated as (potential) acid due to the assumed complete nitrification. $CL(Ac_{pot})$ has been defined to have no deposition terms in its definition, since Bc and Cl deposition are not really an ecosystem property and can (and often do) change over time. However, since these depositions are partly of non-anthropogenic origin (e.g., Saharan dust) and since they are not subject to emission reduction negotiations, they are kept in the critical load definition for convenience.

A further distinction has been made earlier (see, e.g., Sverdrup and De Vries 1994) between 'land use acidity' $Bc_u – N_i – N_u – N_{de}$ and 'soil acidity' which is used to define a so-called critical load of (actual) acidity as:

(5.21)
$$CL(A) = BC_w - ANC_{le,crit}$$

The reason for making this distinction was to exclude all variables that may change in the long term such as uptake of Bc and N, which are influenced by forest management, and N immobilisation and denitrification, which may change due to changes in the hydrological regime. There are two problems with this reasoning: (a) the remaining terms in eq. 5.21 are also liable to change (e.g. ANC leaching depends on precipitation surplus, see below), and (b) uptake and other N processes are a defining part of the ecosystem (vegetation) itself. In other words, $CL(A)$ may be a critical load of *soil* acidity, but it is rarely the soil as such that is the 'sensitive element' to be protected, but the vegetation growing on that soil! Nevertheless, quantities such as $CL(A)$ are computed and reported, and they can have a role as useful short-hand notation for the variables involved.

Note that eq. 5.19 does not give a unique critical load for S or N. However, nitrogen sinks cannot compensate incoming sulphur acidity, and therefore the maximum critical load for sulphur is given by:

(5.22)
$$\begin{aligned} CL_{max}(S) &= BC^*_{dep} - Cl^*_{dep} + BC_w - Bc_u - ANC_{le,crit} \\ &= BC^*_{dep} - Cl^*_{dep} - Bc_u + CL(A) \end{aligned}$$

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

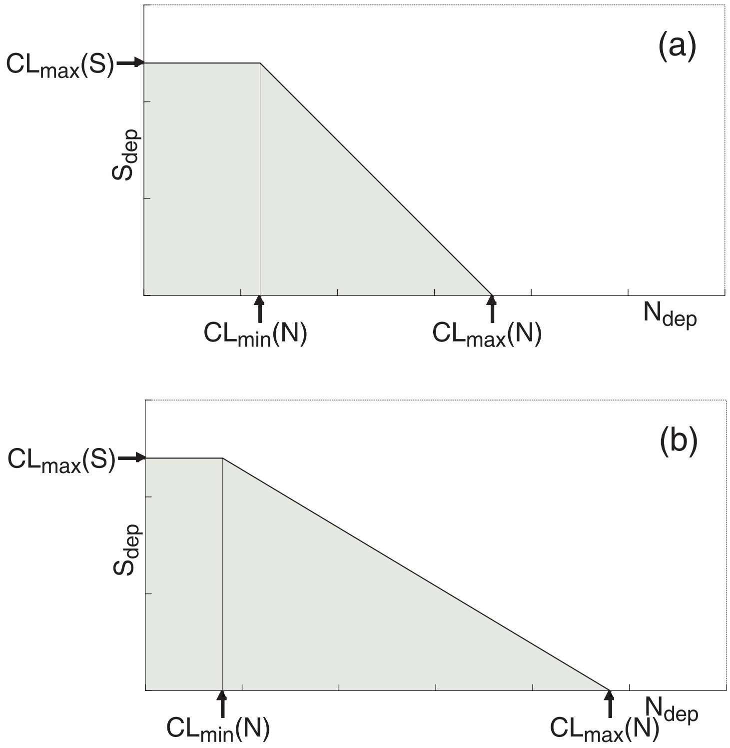

Figure 5.1: Critical load function (CLF) of sulphur and acidifying nitrogen, defined by the three quantities $CL_{max}(S)$, $CL_{min}(N)$ and $CL_{max}(N)$. (a) with constant denitrification N_{de}, and thus a 45° slope of the CLF; (b) with deposition-dependent denitrification, resulting in a smaller $CL_{min}(N)$ and a flatter slope, depending on f_{de}. The grey area below the CLF denotes deposition pairs resulting in an ANC leaching greater than $ANC_{le,crit}$ (non-exceedance of critical loads; see Chapter 7).

(5.23)

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

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

(5.24)

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

The three quantities $CL_{max}(S)$, $CL_{min}(N)$ and $CL_{max}(N)$ define the *critical load function* (CLF; depicted in Figure 5.1a). Every deposition pair (N_{dep},S_{dep}) lying on the CLF are critical loads of acidifying S and N.

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 5.3.1 we consider also the case of denitrification being linearly related to the net input of N. Substituting eq. 5.4 for N_{de} into the equations above results in the following expressions for $CL_{min}(N)$ and $CL_{max}(N)$:

(5.25)

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

and

(5.26)

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

where f_{de} $(0 \le f_{de} < 1)$ is the denitrification fraction; $CL_{max}(S)$ remains the same (eq. 5.22). An example of a critical load function with $f_{de} > 0$ is shown in Figure 5.1b.

5.3.2.2 *Chemical criteria and the critical leaching of Acid Neutralising Capacity*

The leaching of Acid Neutralising Capacity (ANC) is defined in eq. 5.10. In the simplest case bicarbonate (HCO_3) and organic anions $(RCOO)$ are neglected since in general they do not contribute significantly at low pH values. In this case the ANC leaching is given by:

(5.27)

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

where Q is the precipitation surplus in $m^3/ha/yr$ (see Section 5.3.1.3 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 decision in setting the criterion will depend on whether the receptor considered is more sensitive to unfavourable pH conditions or to the toxic effects of aluminium. ANC_{le} can then be calculated by either setting a hydrogen ion criterion (i.e., a critical soil solution pH) and calculating the critical aluminium concentration, or vice versa.

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

(5.28)

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

where K_{gibb} is the gibbsite equilibrium constant (see below). Eq. 5.28 is used to calculate the (critical) Al concentration from a given proton concentration, or vice versa.

Different critical chemical criteria are listed below together with the equations for calculating $ANC_{le,crit}$. 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 aluminium concentration:*

Critical limits for Al have been suggested for forest soils, e.g., $[Al]_{crit}=0.2\ eq/m^3$. These are especially useful for drinking water (ground water) protection, e.g., the EC drinking water standard for $[Al]$ of maximally 0.2 mg/L (about 0.02 eq/m³). $ANC_{le,crit}$ can then be calculated as:

(5.29)

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

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

Most widely used for soils is the connection between soil chemical status and plant response (damage to fine root) via a critical molar ratio of the concentrations of base cations $(Bc=Ca+Mg+K)$ and Al in soil solution, denoted as $(Bc/Al)_{crit}$. 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 Bc (compare eq. 5.13):

(5.30)

$$Al_{le,crit} = 1.5 \cdot \frac{Bc_{le}}{(Bc/Al)_{crit}}$$

The factor 1.5 arises from the conversion of mols to equivalents (assuming K as divalent). Using eqs. 5.27 and 5.28, this yields for the critical ANC leaching:

(5.31)

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

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 leacheate, 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 0.01eq/m³.

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. 5.31 with Ca-terms.

(*c*) *Critical aluminium mobilisation rate:*

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

(5.32)

$$Al_{le,crit} = Al_w$$

where Al_w is the weathering of Al from primary minerals $(eq/ha/yr)$. The weathering of Al can be related to the Bc weathering via:

(5.33)

$$Al_w = p \cdot BC_w$$

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

(5.34)

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

Hydrogen ion criteria:

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

(*a*) *Critical pH:*

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

(5.35)

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

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

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

(5.36)

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

where the factor 0.5 comes from converting mols to equivalents. For organic soils the weathering in eq. 5.36 will probably be negligible $(Bc_w=0)$. Values suggested for $(Bc/H)_{crit}$ are expressed as multiples of $(Bc/Al)_{crit}$, these multiples ranging from 0.3 for deciduous trees and ground vegetation to 1 for spruce and pine (Sverdrup and Warfvinge 1993).

Critical base saturation

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

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

As an example, we consider the description of the exchange between H, Al and $Bc=Ca+Mg+K$ as implemented in the Very Simple Dynamic (VSD) as well as the SAFE model (see Posch et al. 2003a or Chapter 6 on dynamic modelling). For both models the critical concentration $[H]_{crit}$ can be found as a solution of an equation of the type:

(5.37)

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

where the coefficients A, B and the exponent p are given in Table 5.10.

Table 5.10: Coefficients in eq. 5.37 for the Gapon and Gaines-Thomas exchange model.

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

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

In general, eq. 5.37 is non-linear and will have to be solved numerically. Only for the Gapon model and the gibbsite equilibrium ($a=3$, $K_{Alox}=K_{gibb}$) it becomes a linear equation with the solution:

(5.38)

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

with

$$K_{Gap} = \frac{1}{k_{HBc} + k_{AlBc} \cdot K_{gibb}^{1/3}}$$

where k_{HBc} and k_{AlBc} are the two (site-specific) selectivity coefficients describing cation exchange and $[Bc]=Bc_{le}/Q$ as above. $[Al]_{crit}$ is then computed from the gibbsite equilibrium (eq. 5.28) and from that the critical ANC leaching can be obtained via eq. 5.29. Values of selectivity coefficients for a range of (Dutch) soil types and combinations of exchangeable ions are given by De Vries and Posch (2003).

In Figure 5.2 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.

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).

5.3.2.3 Sources and derivation of input data

The obvious sources of input data for calculating acidity critical loads are measurements at the site under consideration. However, in many cases these will not be available. For data on the different N quantities see Section 5.3.1. 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. 5.28) depends on the soil. Table 5.11 presents ranges of K_{gibb} (and $pK_{gibb}=-\log_{10}(K_{gibb}$ in $(mol/L)^{-2})$ as a function of the soil organic matter content. A widely used default value is $K_{gibb}=10^8\ (mol/L)^{-2}=300\ m^6/eq^2$.

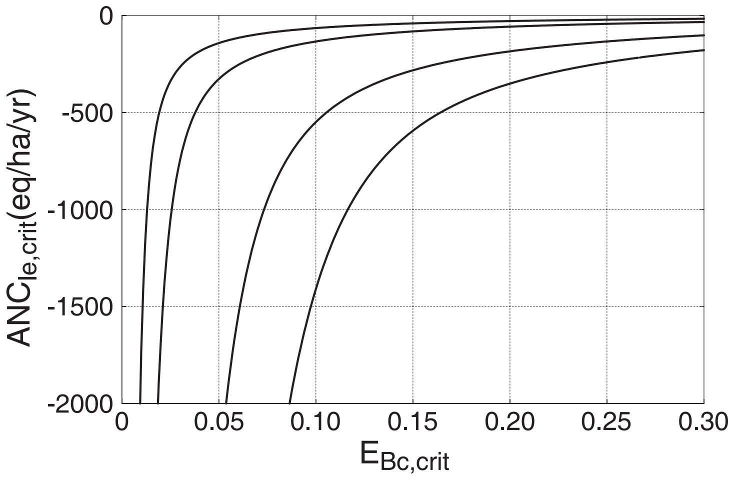

Figure 5.2: Critical ANC leaching (as defined by eq. 5.27, for Q=1 m/yr) as a function of the critical base saturation, $E_{Bc,crit}$, for $[Bc]$=0.02eq/m^3, K_{gibb}=10^8 and K_{Gap}=0.005 (leftmost curve), 0.01, 0.03 and 0.05 (rightmost curve).(To obtain $ANC_{le,crit}$ for arbitrary Q, multiply the values on the vertical axis by Q in m/yr; see also Figure 5.4 below.)

If sufficient empirical data are available to derive the relationship between *[H]* and *[Al]*, these should be used in preference to the gibbsite equilibrium (see Sec. 5.3.2.4).

<u>Base cation and chloride deposition</u>:
The base cation and chloride depositions entering the critical load calculations should be the deposition after all feasible abatement measures have been taken (ideally the non-anthropogenic deposition), and they should be sea-salt corrected. Observations on a European scale are available from the EMEP Chemical Co-ordinating Centre (<u>www.emep.int</u>) or from national sources. See Chapter 2 for more details.

<u>Base cation weathering</u>:
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 5.2.2).

(b) The soil type – texture approximation:
Since mineralogy controls weathering rates, weathering rate classes were assigned to European (forest) soils by De Vries et al. (1993), based on texture class and parent material class. Texture classes are defined in Table 5.12 as a function of their clay and sand content:

Using the FAO soil classification (FAO 1981), the parent material class has been defined for each soil type in Table 5.13 (updated from De Vries et al. 1993).

From texture and parent material class the weathering rate class is obtained from Table 5.14 (modified from De Vries et al. 1993).

Table 5.11: 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

Table 5.12: 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 %

Table 5.13: Parent material classes for common FAO soil types (Posch et al. 2003b).

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.

Table 5.14: Weathering rate classes as a function of texture and parent material classes (Posch et al. 2003b).

	Texture class				
Parent material	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/yr*) for a non-calcareous soil of depth z (in m) is then computed as:

(5.39)

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

where WRc is the weathering rate class (Table 5.14), 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. 5.39.

The above procedure provides weathering rates for $BC=Ca+Mg+K+Na$. However, for computing the critical ANC leaching according to eq. 5.31, the weathering rate for $Bc=Ca+Mg+K$ is needed. Bc_w can be approximated by multiplying Bc_w with a factor between 0.70 for poor sandy soils and 0.85 for rich (sandy) soils. Van der Salm et al. (1998) (for texture classes 2–5, see Table 5.12) and De Vries (1994) (for texture class 1) provide regression equations for weathering rates of Ca, Mg, K and Na as a function of the sand (and silt) content of the soil, which can be used to split Bc_w into individual weathering rates.

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

(5.40)

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

where $(X)_{tot}$ 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 the mineralogy of the site or a total element analysis, from which the 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 CO_2 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 the 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 N (see Section 5.3.1). Average contents of Ca, Mg and K in stems and branches can be found in Table 5.8 (see also Jacobsen et al. 2002). Values have to be multiplied by 2/40.08, 2/24.31 and 1/39.10 for Ca, Mg and K, respectively, to obtain contents in eq/kg.

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

(5.41)
$$Y_u \le Y_{dep} + Y_w - Q \cdot [Y]_{min}$$

for $Y = Ca, Mg, K$

This is preferable to constraining the sum $Bc_u = Ca_u + Mg_u + K_u$ (see eq. 5.31). 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.

5.3.2.4 Possible extensions to the SMB model

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

(a) Generalisation of the Al-H relationship:
In the SMB model the relationship between Al concentration and pH is described as

gibbsite equilibrium (see eq. 5.21). However, Al concentrations, especially in the topsoil, can be influenced by the complexation of Al with organic matter (Cronan et al. 1986, Mulder and Stein 1994). Therefore, the gibbsite equilibrium in the SMB model could be generalised by:

(5.42)

$$[Al] = K_{Alox} \cdot [H]^{a}$$

with equilibrium constant K_{Alox} and exponent a. Obviously, the gibbsite equilibrium is a special case of eq. 5.42 (setting a=3 and $K_{Alox}=K_{gibb}$). The exponent a and K_{Alox} depend on the soil type and especially on the soil horizon. As an example, in Table 5.15 values for K_{Alox} and a are presented for different soil groups and soil depths derived from several hundred Dutch forest soil solution samples (see Van der Salm and De Vries 2001).

The data in Table 5.15 show that a standard gibbsite equilibrium constant and a=3 is reasonable for (Dutch) sandy soils. Very different values, however, are obtained for peat soils and, to a lesser extent, also for loess and clay soils (especially for shallow parts of the soil, where the organic matter content is highest). Data from intensive forest monitoring plots show that there is a strong correlation between a and $\log_{10}K_{Alox}$ (De Vries et al. 2003, p.118), which emphasises that these two parameters cannot be chosen independently.

Figure 5.3 shows the relationship between $[H]$ and $[Al]$ as well as its logarithmic form for different values of K_{Alox} and a. Defining $pX=-\log_{10}[X]$, with $[X]$ given in mol/L, one has $\mathrm{pH}=3-\log_{10}([H])$, if $[H]$ is expressed in eq/m³; and for $[Al]$ in eq/m³ the relationship is $pAl=3-\log_{10}([Al]/3)$.

Note that, when using eq. 5.42 instead of eq. 5.28, 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. 5.9) and the definition of ANC leaching in eq. 5.10 also includes the leaching of bicarbonate anions $(HCO_{3,le}=Q\cdot[HCO_3])$. The concentration of bicarbonates is a function of the pH:

(5.43)

$$[HCO_3] = \frac{K_1 \cdot K_H \cdot p_{CO2}}{[H]}$$

where K_1 is the first dissociation constant, K_H is Henry's constant and p_{CO2} 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 $K_1 \cdot K_H=10^{-1.7}=0.02 eq^2/m^6/atm$. For systems open to the atmosphere, p_{CO2} is about 370 ppm or $3.7\cdot10^{-4}$ atm (in the year 2000). However, in soils p_{CO2} is generally higher (ranging from 10^{-2} to 10^{-1} atm, Bolt and Bruggenwert 1976), due to respiration

Table 5.15: Estimated values of K_{Alox} and the exponent a based on regression between pAl and pH in the soil solution of Dutch forests (N = number of samples).

Soil type	Depth (cm)	$\log_{10} K_{Alox}$ [a)]	a	N
All	humus layer	-1.03	1.17	275
Sandy soils	0–10	3.54	2.26	274
	10–30	5.59	2.68	377
	30–100	7.88	3.13	271
Loess	0–10	-0.38	1.04	45
soils	10–30	3.14	1.83	46
	30–100	4.97	2.21	40
Clay	all depths	4.68	2.15	152
Peat	all depths	1.41	1.85	163

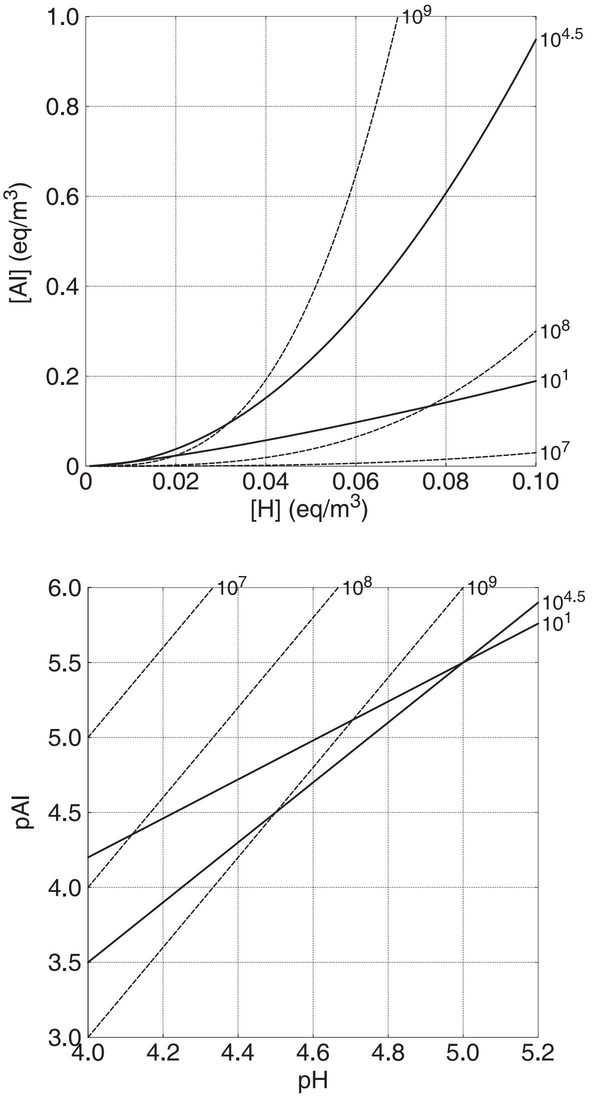

Figure 5.3: Relationships between H and Al concentration in eq/m^3 (left) and in their logarithmic forms (right) for K_{Alox}= 10^1, a=2 and K_{Alox}=$10^{4.5}$, a=1.3 (solid lines) as well as three gibbsite equilibria (a=3) with K_{gibb}=10^7, 10^8 and 10^9 (dashed lines). Note: $[H]$=0.1 eq/m^3 corresponds to pH=4.

and oxidation of below-ground organic matter. Respiratory production of CO_2 is highly temperature dependant (e.g. Witkamp 1966); based on soil temperature and mean growing season soil p_{CO2}, Gunn and Trudgill (1982) derived the following relationship:

(5.44)

$$\log_{10} p_{CO2} = -2.38 + 0.031 \cdot T$$

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

For p_{CO2}=0.0055 atm (about 15 times the partial CO_2 pressure in air) and Q=0.3 m/yr, eq. 5.43 yields a bicarbonate leaching of almost 100 $eq/ha/yr$ at pH=5.5, not always a negligible quantity. Therefore, it would make sense to include the bicarbonate leaching into the SMB model. Not only would this make critical loads more compatible with steady-state solutions of dynamic models, but it is also the only way to allow the ANC leaching to obtain positive values! Eq. 5.27 would than read:

(5.45)

$$\begin{aligned} ANC_{le} &= -H_{le} - Al_{le} + HCO_{3,le} \\ &= Q \cdot ([HCO_3]-[H]-[Al]) \end{aligned}$$

All chemical criteria could be used, since bicarbonate leaching could always be calculated from H_{le} via eq. 5.43. We illustrate the influence of bicarbonates on the ANC leaching by re-drawing Figure 5.2, but now using eq. 5.45 to calculate the ANC leaching. Comparing Figure 5.4 with Figure 5.2 illustrates that, depending on the parameters of the site, bicarbonate leaching can make a significant contribution to the overall ANC leaching.

[c) Including the dissociation of organic acids:

The charge balance (eq. 5.9) and the definition of ANC leaching in eq. 5.10 also include the leaching of organic anions $(RCOO_{le})$. This has been neglected in the SMB model for (at least) two reasons: (i) to keep the SMB model simple, and/or (ii) assuming that the negatively charged organic anion concentration balances the positively charged organic Al-complexes. However, this does not hold for a wide range of pH values, and at sites with high concentrations of organic matter the contribution of organic anions to ANC leaching can be considerable.

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

(5.46)

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

where DOC is the concentration of dissolved organic carbon (in $molC/m^3$), 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 val-

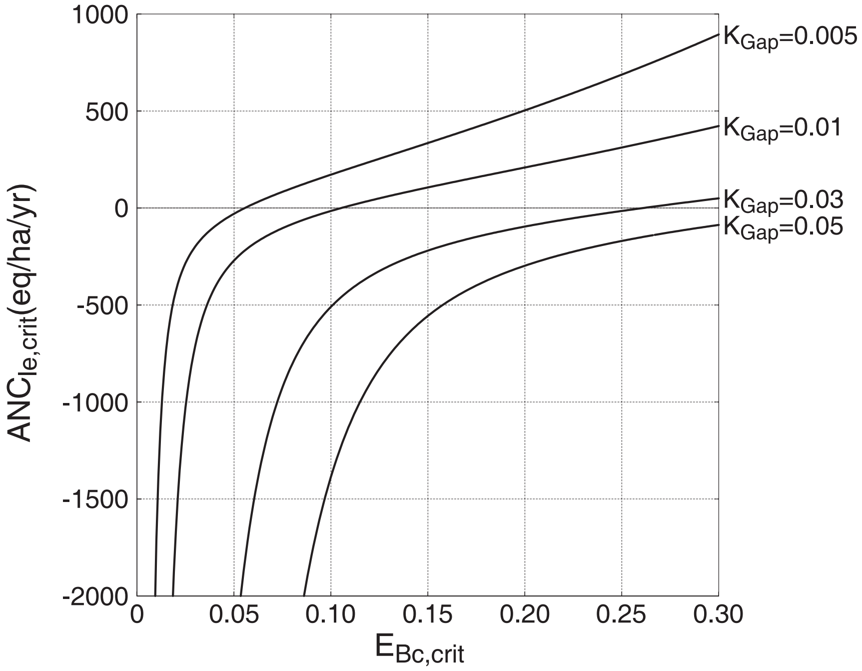

Figure 5.4: Critical ANC leaching (for Q=1 m/yr) *including bicarbonate leaching* as a function of the critical base saturation, $E_{Bc,crit}$, using the same parameters as in Figure 5.2.

ues 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:

(5.47)

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

with a=0.96, b=0.90 and c=0.039 (and m=0.120 mol/molC). Note that eq. 5.47 gives K_1 in mol/L. In Figure 5.5 the fraction of $m \cdot DOC$ 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 5.5 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 $[Al]_{crit}$).

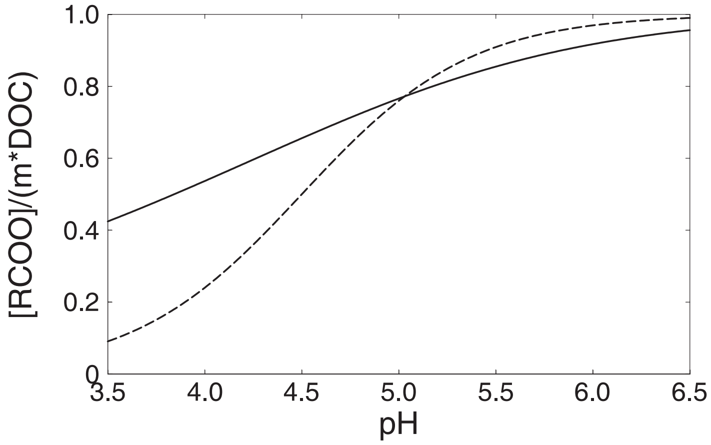

Figure 5.5: Fraction of organic acids $(m\ DOC)$ dissociated as a function of pH for the Oliver model (solid line) and the mono-protic model (eq.5.46) with pK_1=4.5 (dashed line).