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Manual for Dynamic Modelling
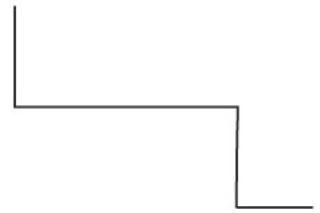# of Soil Response to Atmospheric Deposition

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Working Group on Effects
of the
Convention on Long-range Transboundary Air Pollution

ICP M&M Coordination Center for Effects

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Preface

At the first Expert Workshop on Dynamic Modelling (Ystad, Sweden, 3-5 Oct. 2000) the ICP on Modelling and Mapping was 'urged' to draft a 'Modelling Manual' (UNECE 2001a). A first draft of such a Modelling Manual has been presented at the CCE Workshop (Bilthoven, The Netherlands, April 2001) and the Task Force meeting of the ICP on Modelling and Mapping (Bratislava, Slovakia, May 2001), at which it was recommended to modify the Manual and distribute it for further comments. Further drafts were discussed at the 2nd and 3rd meeting of the Joint Expert Group (JEG) on Dynamic Modelling (Ystad, 6-8 Nov. 2001 and Sitges, Spain, 6-8 Nov. 2002). Its advice, and the advice from several other readers, was taken into account in the preparation of the Manual.

Acknowledgements

Abstract

The objective of this manual is to inform the network of National Focal Centres (NFCs) about the requirements of methodologies for the dynamic modelling of geochemical processes, especially in soils. This information is necessary to support European air quality policies with knowledge on time delays of ecosystem damage or recovery caused by changes, over time, of acidifying deposition.

This Manual has been requested by bodies under the Convention on Long-range Transboundary Air Pollution (CLRTAP) to support the extension of the European critical load database with dynamic modelling parameters.

A Very Simple Dynamic (VSD) model is described to encourage NFCs to meet minimum data requirements upon engaging in the extension of national critical load databases. This manual can be consulted in combination with a running version of VSD, which is available on www.rivm.nl/cce. The report also provides an overview of existing dynamic models, which generally require more input data.

Finally, the manual tentatively describes possible linkages between dynamic modelling results and integrated assessment modelling. This linkage is necessary for use in the near future support of the policy review of the 1999 CLRTAP Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (the 'Gothenburg Protocol') and the 2001 EU National Emission Ceiling Directive.

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Samenvatting

Dit rapport informeert het netwerk van National Focal Centra (NFCs) over de vereisten van methodologiën voor de gevolgtijdelijke (dynamische) modellering van geochemische processen, vooral in bodems. Deze informatie is nodig om het Europese luchtbeleid te kunnen ondersteunen met kennis over tijdsvertragingen van ecosysteemherstel of -schade als gevolg van veranderingen, in de tijd, van verzurende depositie.

Het is geschreven op verzoek van werkgroepen onder de Conventie van Grootschalige Grensoverschrijdende Luchtverontreiniging (CLRTAP). Dit ter ondersteuning van de uitbreiding met dynamische modelparameters van de Europese databank die momenteel uitsluitend kritische waarden voor verzurende en vermestende deposities bevat.

Een Very Simple Dynamic (VSD) model wordt beschreven teneinde NFCs aan te moedigen om te voldoen aan minimale databehoeften bij de uitbreiding van nationale databanken van kritische waarden. De handleiding kan worden geraadpleegd in combinatie met het gebruik van een geïmplementeerde versie van het VSD model dat beschikbaar is op www.rivm.nl/cce. De handleiding geeft ook een overzicht van bestaande dynamische modellen die doorgaans meer complexe databehoeften hebben.

Tenslotte verschaft het rapport een eerste beschrijving van mogelijke verbindingen tussen resultaten van dynamische modellering en geïntegreerde modellen voor de ondersteuning van luchtbeleid (Integrated Assessment Models). Deze zijn in de nabije toekomst nodig voor de ondersteuning van de beleidsmatige evaluatie van het 1999 CLRTAP Protocol voor de bestrijding van verzuring, vermesting en troposferische ozon (het Gotenburg protocol) en de EU-richtlijn 2001/81/EG van het Europese Parlement (2001) inzake nationale emissieplafonds voor bepaalde luchtverontreinigende stoffen (NEC directive).

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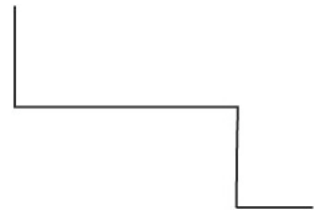
Summary

Dynamic modelling is the logical extension of steady-state critical loads in support of the effects-oriented work under the Convention on Long-range Transboundary Air Pollution (CLRTAP). European data bases and maps of critical loads have been used to support effects-based Protocols to the CLRTAP, such as the 1994 Protocol on Further Reduction of Sulphur Emissions (the 'Oslo Protocol') and the 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (the 'Gothenburg Protocol'). 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. Therefore, in its 17-th session in December 1999, the Executive Body of the Convention '... underlined the importance of ... dynamic modelling of recovery' (ECE/EB.AIR/68 p. 14, para. 51. b) to enable the assessment of 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.

The objective of this Manual is to inform the network of National Focal Centres (NFCs) about the requirements of methodologies for the dynamic modelling of soil and water chemistry. This information has been requested by bodies under the CLRTAP to support the extension of the European critical load database with dynamic modelling parameters. A Very Simple Dynamic (VSD) model is described to encourage NFCs to meet minimum data requirements upon engaging in the extension of national critical load databases. This manual can be read in combination with a running version of VSD, which is available on www.rivm.nl/cce. The manual also provides an overview of existing dynamic models which generally require more input data.

Finally, the manual describes possible linkages between dynamic modelling results and integrated assessment modelling via so-called target load functions. Such a linkage is necessary the future support of the review of the 1999 CLRTAP Gothenburg Protocol and the 2001 EU National Emission Ceiling Directive.

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Contents

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1   Introduction

The critical load concept has been developed in Europe since the mid-1980s, mostly under the auspices of the 1979 Convention on Long-range Transboundary Air Pollution (LRTAP). European data bases and maps of critical loads have been instrumental in formulating effects-based Protocols to the LRTAP Convention, such as the 1994 Protocol on Further Reduction of Sulphur Emissions (the 'Oslo Protocol') and the 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone (the 'Gothenburg Protocol').

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. Therefore, in its 17-th session in December 1999, the Executive Body of the Convention '... underlined the importance of ... dynamic modelling of recovery' (UNECE 1999).

Dynamic models are not new. For 15-20 years scientists have been developing, testing and applying dynamic models to simulate the acidification of soils or surface waters, mostly due to the deposition of sulphur. But it is a relatively new topic for the effects-oriented work under the LRTAP Convention. Earlier work, e.g. under the ICP on Integrated Monitoring, has applied existing dynamic models at a few sites for which sufficient input data are available. The new challenge is to develop and apply dynamic model(s) on a European scale and to combine them as much as possible with the integrated assessment work under the LRTAP Convention, in support of the review and potential revision of protocols.

This Manual aims at providing information for the National Focal Centres (NFCs) of the ICP on Modelling and Mapping and their collaborating institutes on the concepts and data requirements for dynamic modelling. It should assist them in providing information on dynamic model inputs and results to the Coordination Center for Effects (CCE), if and when requested by the Working Group on Effects (WGE). This Manual is *not* a user manual for running any existing dynamic model. Rather, it focuses on those aspects of dynamic modelling relevant to the work under the LRTAP Convention in general and its application in integrated assessment in particular. An important constraint in this context is that any dynamic modelling output generated for this purpose has to be consistent with results from critical loads modelling. For example, in areas, where critical loads were never exceeded, dynamic models should not identify the need for further deposition reductions. With these constraints in mind, this Manual provides a description of basic principles and equations underlying essentially all dynamic soil models as well as the (minimum) input data requirements. Emphasis is placed on consistency and compatibility with the Simple Mass Balance (SMB) model for calculating critical loads. An important part of this Manual is the discussion of the links with integrated assessment (modelling), since this is the main context in which dynamic modelling results will be used under the framework of the LRTAP Convention. It is the hope of the compilers of this Manual that it will do what the Mapping Manual did for critical loads: To help creating common procedures and data bases which can be used in future negotiations on emission reductions of sulphur and nitrogen.

The organisation of the Manual is as follows. Chapter 2 explains the reasons for dynamic modelling in the framework of the Convention on LRTAP as a next step following the assessment of European critical loads and summarises the possible use of dynamic modelling results in integrated assessment. Chapter 3 focuses on the basic concepts and related equations of dynamic modelling and the underlying treatment of finite buffer processes influencing the long-term temporal development of critical limits. Chapter 4 provides a short overview of existing widely used dynamic models, including relevant literature references. Chapter 5 discusses input data and calibration requirements of dynamic models with emphasis on the variables for which data are needed in addition to those needed for critical load calculations. Chapter 6 discusses the problems encountered when calculating target loads and lists a number of options for presenting dynamic modelling results, with emphasis on methods for presenting results on a regional scale. Finally, some special (technical) topics are treated in several Annexes.

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2 Dynamic Modelling in Support of Protocol Negotiations

The purpose of this Chapter is to explain and motivate the use (and constraints) of dynamic modelling as a natural extension of critical loads in support of the effects-oriented work under the LRTAP Convention.

2.1 Why dynamic modelling?

In the Mapping Manual (UBA 1996) the methodologies for calculating critical loads for use under the LRTAP Convention have been documented. Dynamic models have been discussed in workshops of the ICP on Modelling and Mapping since 1989, and the Mapping Manual contains a short section on dynamic modelling (pp.116-121), which mostly summarises the characteristics of some widely used dynamic models. The present Manual can be seen as an extension of that section in the Mapping Manual. 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 separate report dealing with the dynamic modelling of surface waters on a regional scale has been prepared under the auspices of the ICP Waters (Jenkins et al. 2002).

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-ratio[1]) that links the critical load to the (biological) effect(s), immediately attains a non-critical ('safe') value and that there is immediate 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

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[1] In the Mapping Manual (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.

chemical parameter, and it might take decades or even centuries, before an 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. Al/Bc<1), it will take time before biological recovery is achieved.

Figure 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 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 (but see Annex A), damage and recovery delay times mostly refer to chemical recovery alone and this is used as a surrogate for overall recovery.

In addition to the large number of dynamic model applications to individual sites over the past 15 years, there are several examples of early applications of dynamic models on a (large) regional scale. Earlier versions of the RAINS model (Alcamo et al. 1990) contained an effects module which simulated soil acidification on a European scale (Kauppi et al. 1986) and lake acidification in the Nordic countries (Kämäri and Posch 1987). Cosby et al. (1989) applied the MAGIC dynamic lake acidification model to regional lake survey data in southern Norway, and Evans et al. (2001) used the same model to study freshwater acidification and recovery in the United Kingdom. Alveteg et al. (1995) and SAEFL (1998) used the SAFE model to assess temporal trends in soil acidification in southern Sweden and Switzerland. De Vries et al. (1994) employed the SMART model to simulate soil acidification in Europe, and Hettelingh and Posch (1994) used the same model to investigate recovery delay times on a European scale.
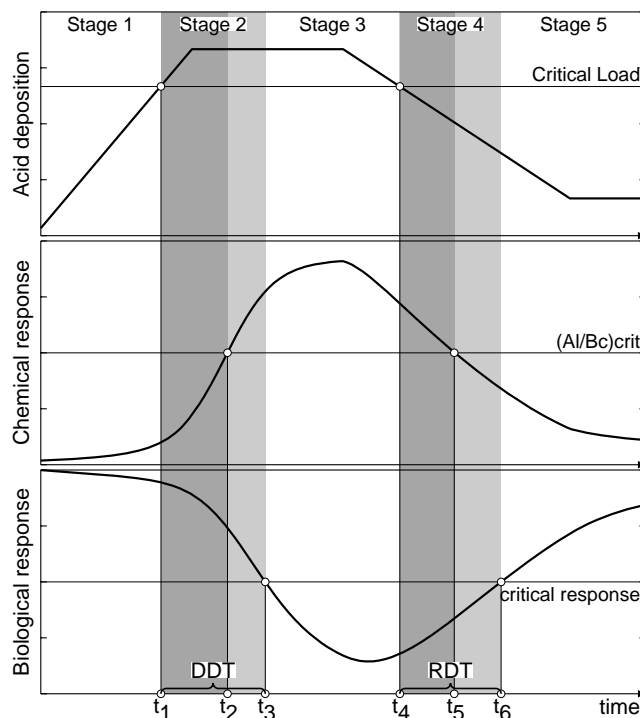
Figure 1: 'Typical' past and future development of the acid deposition effects on a soil chemical variable (Al/Bc-ratio) and the corresponding biological response in comparison to the critical values of those variables and the critical load derived from them. The delay between the (non)exceedance of 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.

The dynamic modelling concepts and data requirements presented in the following are an extension of those employed in deriving the Simple Mass Balance (SMB) model. The SMB model is described in detail in the Mapping Manual. Earlier descriptions of the SMB model can be found in Sverdrup et al. (1990), De Vries (1991), Sverdrup and De Vries (1994) and Posch et al. (1995). The most basic extension of the SMB model into a dynamic soil acidification model are realised in the Very Simple Dynamic (VSD) model, which is described in Posch and Reinds (2003).

2.2   Steady state and dynamic models

Steady-state models (critical loads) have been used to negotiate emission reductions in Europe. An emission reduction will be 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 the dynamic models to be used in the assessment of recovery under the LRTAP Convention have to 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 have to 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, the steady-state version of the dynamic model used has to be the SMB (e.g. the SMART model). Analogously, if the SAFE model is used for dynamic simulations, critical loads have to be calculated with the steady-state PROFILE model; etc.

Most likely, due to a lack of (additional) data and other resources, it will be impossible to run dynamic models on all sites in Europe for which critical loads are calculated at present (about 1.5 million). However, the selection of the subset or sub-regions of sites, at which dynamic models are applied in support of integrated assessments, has to be representative enough to allow comparison with results obtained with critical loads.

Dynamic models of acidification are based on the same principles as steady-state models: The charge balance of the ions in the soil solution, mass balances of the various ions, and equilibrium equations. However, whereas in steady-state models only infinite sources and sinks are considered (such as base cation weathering), the inclusion of the finite sources and sinks of major ions into the structure of dynamic models is crucial, since they determine the long-term (slow) changes in soil (solution) chemistry. The three most important processes involving finite buffers and time-dependent sources/sinks are cation exchange, nitrogen retention and sulphate adsorption.

Cation exchange is characterised by two quantities: cation exchange capacity (CEC), the total number of exchange sites (a soil property), and base saturation, the fraction of those sites occupied by base cations at any given time. After an increase in acidifying input, cation exchange (initially) delays the decrease in the acid neutralisation capacity (ANC) by releasing base cations from the exchange complex, thus delaying the acidification of the soil solution until a new equilibrium is reached (at a lower base saturation). On the other hand, cation exchange delays recovery since 'extra' base cations are needed to replenish base saturation instead of increasing the ANC of the soil solution. Detailed discussions and early model formulations of cation exchange reactions in the context of soil acidification can be found in Reuss (1980, 1983) and Reuss and Johnson (1986).

Finite nitrogen sinks: In the calculation of critical loads the net input of nitrogen is assumed constant over time or, in case of denitrification, a function of the (constant) N deposition. However, it is well known that the amount of N immobilised is in most cases larger than the long-term sustainable ('acceptable') immobilisation rate used in critical load calculations. Observational and experimental evidence (e.g. Gundersen et al. 1998a) shows a correlation between the C/N-ratio and the amount of N retained in the soil organic layer. This correlation can been used to formulate simple models of N immobilisation in which the amount of N retained is a function of the prevailing C/N-ratio, which in turn is updated by the amount retained. Such an approach is described below and used in the SMART model (De Vries et al. 1994), the MERLIN model (Cosby et al. 1997) and in version 7 of the MAGIC model (Cosby et al. 2001).

Sulphate adsorption can be an important process in some soils for regulating sulphate concentration in the soil solution. Equilibrium between dissolved and adsorbed sulphate in the soil/soilwater system is typically described by a Langmuir isotherm, which is characterised by two parameters: The maximum adsorption capacity and the 'half-saturation constant', which determines the speed of the response to changes in sulphate concentration. A description and extensive model experiments can be found in Cosby et al. (1986).

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2.3   Use of dynamic models in Integrated Assessment

Ultimately, within the framework of the LRTAP Convention, a link has to be established between the dynamic soil models and integrated assessment (models) used in the Task Force on Integrated Assessment Modelling (TFIAM). The following modes of interaction with integrated assessment (IA) models can be identified:

Scenario analyses:
Deposition scenario output from IA models are used by the 'effects community' (ICPs) as input to dynamic models to analyse their impact on (European) soils and surface waters, and the results (recovery times etc.) are reported back to the 'IA community'.

Presently available dynamic models are well suited for this task. The question is how to summarise the resulting information on a European scale. Also, the 'turn-around time' of such an analysis, i.e. the time between obtaining deposition scenarios and reporting back dynamic model results, is bound to be long within the framework of the LRTAP Convention.

Response functions for optimisation (e.g. target load functions):
Response functions are derived with dynamic models and linked to IA models. Such response functions encapsulate a site's temporal behaviour to reach a certain (chemical) state in response to a broad range of (future) deposition patterns; or they characterise the amount of deposition reductions needed to obtain a certain state within a prescribed time.

In the first case these response functions are pre-processed model runs for a large number of plausible future deposition patterns from which the results for every (reasonable) deposition scenario can be obtained by interpolation. A first attempt in this direction has been presented by Alveteg et al. (2000); and an example is shown in Figure 2. It shows the isolines of years ('recovery isochrones') in which Al/Bc<1 is attained for the first time for a given combination of percent deposition reduction (vertical axis) and implementation year (horizontal axis). The reductions are expressed as percentage of the deposition in 2010 after implementation of the Gothenburg Protocol and the implementation year refers to the full implementation of that additional reduction. For example, a 48% reduction of the 2010 deposition, fully implemented by the year 2030 will result in a (chemical) recovery by the year 2060 (dashed line in Figure 2). Note that for this example site, at which critical loads are still exceeded after implementation of the Gothenburg Protocol, no recovery is possible unless further reductions exceed 32% of the 2010 level.
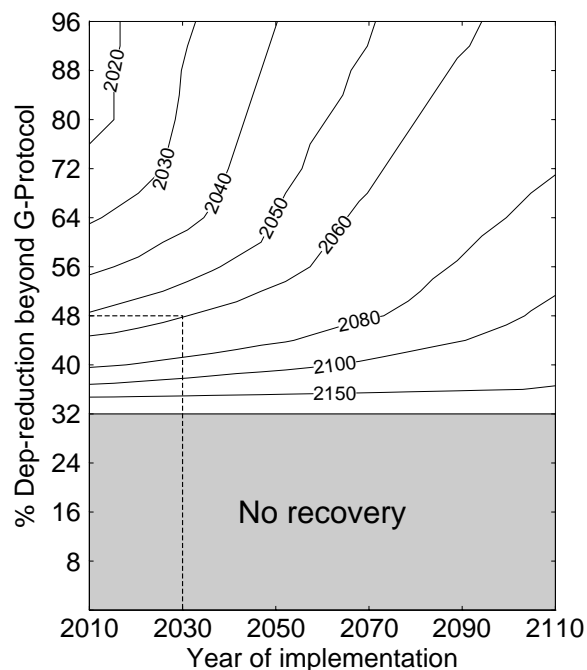
Figure 2: Example of 'recovery isochrones'. The vertical axis gives the additional reduction in acidifying deposition *after* the implementation of the Gothenburg Protocol in 2010 (expressed as percentage of the 2010 level) and the horizontal axis the year at which this additional reductions are fully implemented. The isolines are labelled with the first year at which Al/Bc<1 is attained for a given combination of percent reduction and implementation year.

Considering how critical loads have been used in IA during the negotiations of protocols, it is unlikely that there will be much discussion about the implementation year of a new reduction agreement (mostly 5-10 years after a protocol enters into force). Thus the question will be: What is the maximum deposition allowed to obtain (and sustain!) a desired chemical state (e.g. Al/Bc=1) in a prescribed year? In the case of a single pollutant, this can be read from information as presented in Figure 2. However, in the case of acidity, both N and S deposition determine the soil chemical state. In addition, it will not be possible to obtain unique pairs of N and S deposition to reach a prescribed target (compare critical load function for acidity critical loads). Thus, dynamic models are used to determine **target loads functions** for a series of target years. These target load functions, or suitable statistics derived from them, are passed on to the IA-modellers who evaluate their feasibility of achievement (in terms of costs and technological abatement options available). In Figure 3 examples of target load functions are shown for a set of target years.

The determination of target load functions (or any other type of response functions) requires no changes to existing models *per se*, but rather additional work, since dynamic soil model have to run many times and/or 'backwards', i.e. in an iterative mode. A further discussion of the problems and possible pitfalls in the computation of target load functions can be found in Chapter 6.

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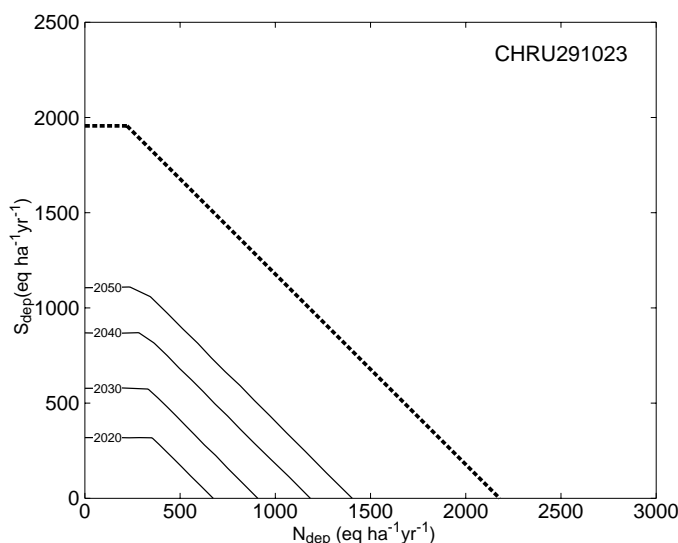
Figure 3: Examples of target load functions for 4 different target years (2020-2050). Also shown is the critical load function of the site (thick dashed line). Note that any target load function has to lie below the critical load function, i.e. requires stricter deposition reductions than achieving critical load.

Integrated dynamic model:
A dynamic model could be integrated into the IA models (e.g. RAINS) and used in scenario analyses and optimisation runs. The widely used models, such as MAGIC, SAFE and SMART, are not easily incorporated into IA models, and they might be still too complex to be used in optimisation runs. Alternatively, the VSD model could be incorporated into the IA models, capturing the essential, long-term features of dynamic soil models. This would be comparable to the process that led to the simple ozone model included in RAINS, which was derived from the complex photo-oxidant model of EMEP. However, even this would require a major effort, not the least of which is the creation of a European database to run the model.

2.4 Constraints for dynamic modelling under the LRTAP Convention

The request of the Executive Body for dynamic model applications is aimed in particular at regions where critical loads are exceeded even after the implementation of the Gothenburg Protocol. For these regions policy questions include *when* damage becomes irreversible or *how* additional emission reductions can be best phased in. But also regions where exceedances no longer occur are of interest. In such regions policy questions include *when* recovery is achieved (see also Warfvinge et al. 1992). Therefore, an important constraint for the application of dynamic modelling is that the input database for a European application – including the chosen critical limit(s) – is compatible with the input data for critical loads submitted by NFCs. Otherwise dynamic model applications may not result in the same regional patterns of exceedances, which would be highly confusing for the review process of the Gothenburg Protocol. On the other hand, the extension of the current critical load database to enable the application of dynamic models provides an excellent opportunity to review and update national critical load databases.

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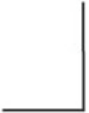
3   Basic Concepts and Equations

In this chapter we present the basic concepts and equations common to virtually all dynamic (soil) models and discuss the underlying simplifying assumptions. The guiding principle is the compatibility with critical load models, since the steady-state solutions of the dynamic model employed should be the critical loads.

In addition to chemical criteria, which have been used to set critical loads and will thus be used to define/judge recovery, also the biological response has to be considered. And although models for that are largely lacking, some ideas are presented in Annex A.

3.1   Basic equations

As mentioned above, we consider as 'ecosystem' non-calcareous forest soils, although most of the considerations hold also for non-calcareous soils covered by (semi-)natural vegetation. Since we are interested in applications on a large regional scale (for which data are scarce) and long time horizons (decades to centuries with a time step of one year), we assume that the soil is a single homogeneous compartment and its depth is equal to the root zone. This implies that internal soil processes (such as weathering and uptake) are evenly distributed over the soil profile, and all physico-chemical constants are assumed uniform in the whole profile. Furthermore we assume the simplest possible hydrology: The water leaving the root zone is equal to precipitation minus evapotranspiration; more precisely, percolation is constant through the soil profile and occurs only vertically. These are the same assumptions made when deriving critical loads with the Simple Mass Balance (SMB) model.

As for the SMB model, the starting point is the charge balance of the major ions in the soil water, leaching from the root zone:

$$(3.1) \quad SO_{4,le} + NO_{3,le} - NH_{4,le} - BC_{le} + Cl_{le} = H_{le} + Al_{le} - HCO_{3,le} - RCOO_{le} = -ANC_{le}$$

where BC=Ca+Mg+K+Na and RCOO stands for the sum of organic anions. Eq.3.1 also defines the acid neutralising capacity, ANC. The leaching term is given by $X_{le}=Q[X]$ where $[X]$ is the soil solution concentration (eq/m^3) of ion X and Q (m/yr) is the water percolating from the root zone (precipitation minus evapotranspiration). All quantities are expressed in equivalents (moles of charge) per unit area and time (e.g. eq/m^2/yr).

The concentration $[X]$ of an ion in the soil compartment, and thus its leaching X_{le} in the charge balance, is related to the sources and sinks of X via a mass balance equation, which describes the change over time of the total amount of ion X per unit area in the soil matrix/soil solution system, X_{tot} (eq/m^2):

$$(3.2) \quad \frac{d}{dt}X_{tot} = X_{net} - X_{le}$$

where X_{net} (eq/m^2/yr) is the net input of ion X (sources minus sinks, except leaching), which are specified and discussed below.

With the simplifying assumptions used in the derivation of the SMB model, the net input of sulphate and chloride is given by their respective deposition:

$$(3.3) \qquad SO_{4,net} = S_{dep} \quad \text{and} \quad Cl_{net} = Cl_{dep}$$

For base cations the net input is given by (Bc=Ca+Mg+K, BC=Bc+Na):

$$(3.4) \qquad BC_{net} = BC_{dep} + BC_w - Bc_u$$

where the subscripts *dep*, *w* and *u* stand for deposition, weathering and net uptake, respectively. Note, that S adsorption and cation exchange reactions are not included here, they are included in X_{tot} and described by equilibrium equations (see below). For nitrate and ammonium the net input consists of (at least) deposition, nitrification, denitrification, net uptake and immobilisation:

$$(3.5) \qquad NO_{3,net} = NO_{x,dep} + NH_{4,ni} - NO_{3,i} - NO_{3,u} - NO_{3,de}$$

$$(3.6) \qquad NH_{4,net} = NH_{3,dep} - NH_{4,ni} - NH_{4,i} - NH_{4,u}$$

where the subscripts *ni*, *i* and *de* stand for nitrification, net immobilisation and denitrification, respectively. In the case of complete nitrification one has $NH_{4,net}$=0 and the net input of nitrogen is given by:

$$(3.7) \qquad NO_{3,net} = N_{net} = N_{dep} - N_i - N_u - N_{de}$$

In addition to the mass balances, equilibrium equations describe the interaction of the soil solution with air and the soil matrix. The dissolution of (free) Al is modelled by the following equation:

$$(3.8) \qquad [Al] = KAl_{ox}[H]^{\alpha}$$

where $\alpha>0$ is a site-dependent exponent. For α=3 this is the familiar gibbsite equilibrium ($KAl_{ox}=K_{gibb}$).

Bicarbonate ions were neglected in the derivation of the SMB model since for low pH-values related to the critical limit for forest soils the resulting error was considered negligible. But they can as easily be included: The bicarbonate concentration, $[HCO_3]$, is computed as

$$(3.9) \qquad [HCO_3] = \frac{K_1 K_H p_{CO2}}{[H]}$$

where K_1 is the first dissociation constant, K_H is Henry's constant ($K_1 K_H$=$10^{-1.7}$=0.02 eq^2/m^6/atm at 8°C) and p_{CO2} (atm) is the partial pressure of CO_2 in the soil solution. Note that the inclusion of bicarbonates into the charge balance is necessary, if the ANC is to attain positive values.

Also organic anions have been neglected in the critical load calculations, the assumption being that all organic anions are complexed with aluminium, i.e. free Al is equal to total Al minus

organic anions. But as long as they are modelled by equilibrium equations with $[H]$ their inclusion does not pose any difficulty.

Thus the ANC-concentration can be expressed as a function of $[H]$ alone (see eq.3.1):

(3.10)
$$\begin{aligned} ANC([H]) &= F_{org}([H]) + \frac{K_1 K_H p_{CO2}}{[H]} - [H] - KAl_{ox}[H]^\alpha \\ &= [BC] - [SO_4] - [N] - [Cl] \end{aligned}$$

where F_{org} is a function expressing organic anion concentration(s) in terms of $[H]$.

3.2   Finite buffer processes

Finite buffers have not been included in the derivation of critical loads, since they do not influence the steady state. However, when investigating the chemistry of soils over time as a function of changing deposition patterns, these finite buffers govern the long-term (slow) changes in soil (solution) chemistry. These finite buffers include adsorption/desorption processes, mineralisation/immobilisation processes and dissolution/precipitation processes, and in the following we discuss them in turn.

3.2.1   Sources and sinks of cations

Cation exchange:
Generally, the solid phase particles of a soil carry an excess of cations at their surface layer. Since electro-neutrality has to be maintained, these cations cannot be removed from the soil, but they can be exchanged against other cations, e.g. those in the soil solution. This process is known as cation exchange; and every soil (layer) is characterised by the total amount of exchangeable cations per unit mass (weight), the so-called cation exchange capacity (CEC, measured in meq/kg). If X and Y are two cations with charges m and n, then the general form of the equations used to describe the exchange between the liquid-phase concentrations (or activities) $[X]$ and $[Y]$ and the equivalent fractions E_X and E_Y at the exchange complex is

(3.11)
$$\frac{E_X^i}{E_Y^j} = K_{XY} \frac{[X^{m+}]^n}{[Y^{n+}]^m}$$

where K_{XY} is the so-called exchange (or selectivity) constant, a soil-dependent quantity. Depending on the powers i and j different models of cation exchange can be distinguished: For $i=n$ and $j=m$ one obtains the Gaines-Thomas exchange equations, whereas for $i=j=mn$, after taking the mn-th root, the Gapon exchange equations are obtained.

The number of exchangeable cations considered depends on the purpose and complexity of the model. For example, Reuss (1983) considered only the exchange between Al and Ca (or divalent base cations). In general, if the exchange between N ions is considered, $N–1$, exchange equations (and constants) are required, all the other $(N–1)(N–2)/2$ relationships and constants can be easily derived from them. In the VSD model the exchange between aluminium, divalent base cations and protons is considered. The exchange of protons is

important, if the cation exchange capacity (CEC) is measured at high pH-values (pH=6.5). In the case of the Bc-Al-H system, the Gaines-Thomas equations read:

$$(3.12) \qquad \frac{E_{Al}^2}{E_{Bc}^3} = K_{AlBc} \frac{[Al^{3+}]^2}{[Bc^{2+}]^3} \qquad \text{and} \qquad \frac{E_H^2}{E_{Bc}} = K_{HBc} \frac{[H^+]^2}{[Bc^{2+}]}$$

where Bc=Ca+Mg+K, with K treated as divalent. The equation for the exchange of protons against Al can be obtained from eqs.3.12 by division:

$$(3.13) \qquad \frac{E_H^3}{E_{Al}} = K_{HAl} \frac{[H^+]^3}{[Al^{3+}]} \qquad \text{with} \qquad K_{HAl} = \sqrt{K_{HBc}^3 / K_{AlBc}}$$

The corresponding Gapon exchange equations read:

$$(3.14) \qquad \frac{E_{Al}}{E_{Bc}} = k_{AlBc} \frac{[Al^{3+}]^{1/3}}{[Bc^{2+}]^{1/2}} \qquad \text{and} \qquad \frac{E_H}{E_{Bc}} = k_{HBc} \frac{[H^+]}{[Bc^{2+}]^{1/2}}$$

Again, the H-Al exchange can be obtained by division (with $k_{HAl}=k_{HBc}/k_{AlBc}$). Charge balance requires that the exchangeable fractions add up to one:

$$(3.15) \qquad E_{Bc} + E_{Al} + E_H = 1$$

The user of the VSD model can choose between the Gaines-Thomas and the Gapon Bc-Al-H exchange model. The sum of the fractions of exchangeable base cations (here E_{Bc}) is called the *base saturation* of the soil; and it is the time development of the base saturation, which is of interest in dynamic modelling. In the above formulations the exchange of Na, NH_4 (which can be important in high NH_4 deposition areas) and heavy metals is neglected (or subsumed in the proton fraction).

Care has to be exercised when comparing models, since different sets of exchange equations are used in different models. Whereas eqs.3.12 are used in the SMART model (but with Ca+Mg instead of Bc, K-exchange being ignored in the current version), the SAFE model employs the Gapon exchange equations (eqs.3.14), however with exchange constants $k'_{X/Y}=1/k_{XY}$. In the MAGIC model the exchange of Al with all four base cations is modelled separately with Gaines-Thomas equations, without explicitly considering H-exchange. In Chapter 5 ranges of values for the exchange constants for the different model formulations are presented.

3.2.2 Sources and sinks of nitrogen

Mineralisation and immobilisation:
Several models do include descriptions for mineralisation and immobilisation, following e.g. first order kinetics or Michaelis-Menten kinetics. For those descriptions we refer to the respective models. In its most simple form, a net immobilisation of nitrogen is included, being the difference between mineralisation and immobilisation.

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In the calculation of critical loads the (acceptable, sustainable) long-term net immobilisation $N_{i,acc}$, is assumed to be constant and not influencing the C/N-ratio, i.e. a proportional amount of C is assumed to be immobilised. However, it is well known, that the amount of N immobilised is (at present) in many cases larger than this long-term value. Thus a submodel describing the nitrogen dynamics in the soil is part of most dynamic models. For example, the MAKEDEP model (Alveteg et al. 1998a, Alveteg and Sverdrup 2002), which is part of the SAFE model system (but can also be used as a stand-alone routine) describes the N-dynamics in the soil as a function of forest growth and deposition.

According to Dise et al. (1998) and Gundersen et al. (1998b) the forest floor C/N-ratios may be used to assess risk for nitrate leaching. Gundersen et al. (1998b) suggested threshold values of >30, 25 to 30, and <25 to separate low, moderate, and high nitrate leaching risk, respectively. This information has been used in several models, such as SMART (De Vries et al. 1994, Posch and De Vries 1999) and MAGIC (Cosby et al. 2001) to calculate nitrogen immobilisation as a fraction of the net N input, linearly depending on the C/N-ratio. In these models, the C/N-ratio of the mineral topsoil is used.

Between a maximum, CN_{max}, and a minimum C/N-ratio, CN_{min}, the net amount of N immobilised is a linear function of the actual C/N-ratio, CN_t:

$$(3.16) \qquad N_{i,t} = \begin{cases} N_{in,t} & \text{for} & CN_t \geq CN_{max} \\ \dfrac{CN_t - CN_{min}}{CN_{max} - CN_{min}} \cdot N_{in,t} & \text{for} & CN_{min} < CN_t < CN_{max} \\ 0 & \text{for} & CN_t \leq CN_{min} \end{cases}$$

where $N_{in,t}$ is the available N (e.g., $N_{in,t}=N_{dep,t}-N_{u,t}-N_{i,acc}$). At every time step the amount of immobilised N is added to the amount of N in the top soil, which in turn is used to update the C/N-ratio. The total amount immobilised at every tine step is then $N_i=N_{i,acc}+N_{i,t}$. The above equation states that when the C/N-ratio reaches a (pre-set) minimum value, the annual amount of N immobilised equals the acceptable value $N_{i,acc}$ (see Figure 4). This formulation is compatible with the critical load formulation for $t \rightarrow \infty$.
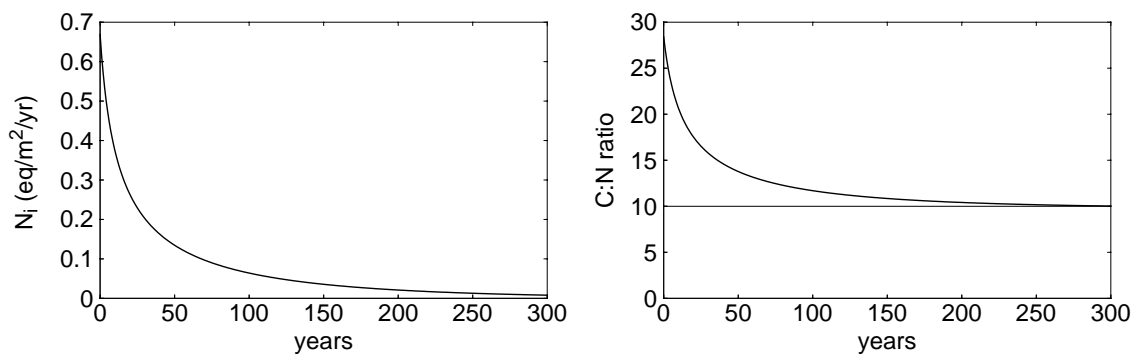
Figure 4: Amount of N immobilised (left) and resulting C/N-ratio in the topsoil (right) for a constant net input of N of 1 eq/m²/yr (initial C_{pool}=5 kgC/m²).

It should be noted that eq.3.16 does not capture all the features of observed (and expected!) behaviour of nitrogen immobilisation in soils, such as 'sudden breakthrough' after saturation, and more research is needed in this area.

3.2.3   Sources and sinks of sulphur

Mineralisation and immobilisation:
Several models do include descriptions for mineralisation and immobilisation, following e.g. first order kinetics or Michaelis-Menten kinetics. For those descriptions, refer to the respective models. In its most simplified form, a net immobilisation of sulphur is included, being the difference between mineralisation and immobilisation, which, in turn, is generally set to zero.

Sulphate adsorption:
The amount of sulphate adsorbed, $SO_{4,ad}$ (meq/kg), is often assumed to be in equilibrium with the solution concentration and is typically described by a Langmuir isotherm (e.g., Cosby et al. 1986):

$$(3.17) \qquad SO_{4,ad} = \frac{[SO_4]}{S_{1/2} + [SO_4]} \cdot S_{max}$$

where S_{max} is the maximum adsorption capacity of sulphur in the soil (meq/kg) and $S_{1/2}$ the half saturation concentration (eq/m^3).

3.3   Critical limits

Chemical criteria:
Using the equations given in section 3.1 the leaching of ANC from the bottom of the root zone can be calculated for any given deposition. However, critical loads are derived by setting a certain soil chemical variable, which connects soil solution chemistry to a 'harmful effect' (the chemical 'criterion'), and by solving the equation 'backwards' to obtain allowable deposition values. The various chemical criteria are summarised in the Mapping Manual and the most frequently used ones are given in Table 1.

Table 1: *Most frequently used chemical criteria (used to derive critical loads).*

Element	Soil solution	Surface water
Acidity	Al/(Ca+Mg+K) < 0.5-2.0	[ANC] > 0-0.05 eq.m^{-3}
Nitrogen	[N] < 0.02-0.04 eq.m^{-3}	[N] < 0.16 mol.m^{-3}

Finite buffers, such as cation exchange capacity, are not considered in the derivation of critical loads, since they do not influence steady-state situations. However, this does *not* mean that the state of those buffers is not influenced by the steady state! The relationship between the base saturation (i.e. the fraction of exchangeable base cations) and the soil chemical variables usually used in critical load calculations, e.g. the Al/Bc-ratio, can be easily derived (see Annex B). This also allows base saturation to be used as a chemical criterion in critical load calculations, as recommended at a recent workshop (Hall et al. 2001, UNECE 2001b).

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Biological response models:

The abiotic models described above focus on the delays between changes in acid deposition and changes in soil and/or surface water chemistry. But there are also delays between changes in chemistry and the biological response. Since the goal of deposition reductions is to restore healthy and sustainable populations of key indicator organisms, the time lag in response is the sum of the delays in chemical and biological response (see also the discussion for Figure 1). Consequently, dynamic models for biological response are needed; and information about such models is given in Annex A, including both steady-state models (regression relationships) and process-oriented dynamic response models.

3.4 From steady state (critical loads) to dynamic simulations

3.4.1 Steady-state calculations

Steady state means there is no change over time in the total amounts of ions involved, i.e. (see eq.3.2):

$$(3.18) \qquad \frac{d}{dt}X_{tot} = 0 \quad \Rightarrow \quad X_{le} = X_{net}$$

From eq.3.5 the critical load of nutrient nitrogen, $CL_{nut}(N)$, is obtained by specifying an acceptable N-leaching, $N_{le(acc)}$. By specifying a critical leaching of ANC, $ANC_{le(crit)}$, and inserting eqs.3.3-3.5 into the charge balance (eq.3.1), one obtains the equation describing the **critical load function** of S and N acidity, from which the three quantities $CL_{max}(S)$, $CL_{min}(N)$ and $CL_{max}(N)$ can be derived (see Mapping Manual).

3.4.2 Dynamic calculations

To obtain time-dependent solutions of the mass balance equations, the term X_{tot} in eq.3.2, i.e. the total amount (per unit area) of ion X in the soil matrix/soil solution system has to be specified. For ions, which do not interact with the soil matrix, X_{tot} is given by the amount of ion X in solution alone:

$$(3.19) \qquad X_{tot} = \Theta z [X]$$

where z (m) is the soil depth under consideration (root zone) and Θ (m^3/m^3) is the (annual average) volumetric water content of the soil compartment. The above equation holds for chloride. For every base cation Y participating in cation exchange, Y_{tot} is given by:

$$(3.20) \qquad Y_{tot} = \Theta z [Y] + \rho z CEC \cdot E_Y$$

where ρ is the soil bulk density (g/cm^3), CEC the cation exchange capacity (meq/kg) and E_Y is the exchangeable fraction of ion Y.

For nitrogen an update of the C/N-ratio is needed in those models which use that ratio in calculating N immobilisation. In this case, N_{tot} is given as:

$$(3.21) \qquad N_{tot} = \Theta\, z\,[N] + \rho\, z N_{soil}$$

If there is no ad/desorption of sulphate, $SO_{4,tot}$ is given by eq.3.19. If sulphate adsorption cannot be neglected, it is given by (see eq.3.17):

$$(3.22) \qquad SO_{4,tot} = \Theta\, z\,[SO_4] + \rho\, z SO_{4,ad}$$

Inserting these expressions into eq.3.2 and observing that $X_{le}=Q[X]$, one obtains differential equations for the temporal development of the concentration of the different ions. Only in the simplest cases can these equations be solved analytically. In general, the mass balance equations are discretised and solved numerically, with the solution algorithm dependent on the model builders' preferences.

When the rate of Al leaching is greater than the rate of Al mobilisation by weathering of primary minerals, the remaining part of Al has to be supplied from readily available Al pools, such as Al hydroxides. This causes depletion of these minerals, which might induce an increase in Fe buffering which in turn leads to a decrease in the availability of phosphate (De Vries 1994). Furthermore, the decrease of those pools in podzolic sandy soils may cause a loss in the structure of those soils. The amount of aluminium is in most models assumed to be infinite and thus no mass balance for Al is considered. The SMART model, however, includes an Al balance, and the terms in eq.3.2 are $Al_{net}=Al_w$ and Al_{tot} is given by

$$(3.23) \qquad Al_{tot} = \Theta\, z\,[Al] + CEC_a E_{Al} + \rho z Al_{ox}$$

where Al_{ox} (meq/kg) is the amount of oxalate extractable Al, the pool of readily available Al in the soil.

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4   Available Dynamic Models

In the previous sections the basic processes involved in soil acidification have been summarised and expressed in mathematical form, with emphasis on slow (long-term) processes. The resulting equations, or generalisations and variants thereof, together with appropriate solution algorithms and input-output routines have over the past 15 years been packaged into soil acidification models, mostly known by their (more or less fancy) acronyms.

There is no shortage of soil (acidification) models, but most of them are not designed for regional applications. A comparison of 16 models can be found in a special issue of the journal 'Ecological Modelling' (Tiktak and Van Grinsven 1995). These models emphasise either soil chemistry (such as SMART, SAFE and MAGIC) or the interaction with the forest (growth). There are very few truly integrated forest-soil models. An example is the forest model series ForM-S (Oja et al. 1995), which is implemented not in a 'conventional' Fortran code, but is realised in the high-level modelling software STELLA.

The following selection is biased towards models which have been (widely) used and which are simple enough to be applied on a (large) regional scale. Only a short description of the models can be given, but details can be found in the references cited. It should be emphasised that the term 'model' used here refers, in general, to a model system, i.e. a set of (linked) software (and databases) which consists of pre-processors for input data (preparation) and calibration, post-processors for the model output, and – in general the smallest part – the actual model itself.

An overview of the various models is given in Table 2. The first three models are soil models of increasing complexity, whereas the MAGIC model is generally applied at the catchment level. Application on the catchment level, instead on a single (forest) plot, has implications for the derivation of input data. E.g., weathering rates have to represent the average weathering of the whole catchment, data that is difficult to obtain from soil parameters. Thus in MAGIC catchment weathering is calibrated from water quality data.

Table 2: Overview of dynamic models (which have been applied on a regional scale).

Model	Essential process descriptions	Layers	Essential model inputs	Contact
VSD	ANC charge balance Mass balances for BC and N (complete nitrification assumed)	One	CL input data + CEC, base saturation C/N-ratio	Max Posch
SMART	VSD model + SO_4 sorption Mass balances for $CaCO_3$ and Al Separate mass balances for NH_4 and NO_3, nitrification Complexation of Al with DOC	One	VSD model + S_{max} and $S_{1/2}$ Ca-carbonate, Al_{ox} Nitrification fraction, f_{ni} pK values	Wim de Vries

SAFE	VSD model +
	Separate weathering calculation
	Element cycling by litterfall,
	  root decay,
	  mineralisation and root uptake
		Several	VSD model +
			Input data for PROFILE
			Litterfall rate,
			parameters describing
			mineralisation and root uptake
				Harald Sverdrup

MAGIC	VSD model +	Several(m	VSD model +	Dick Wright
	SO_4 sorption	ostly one)	S_{max} and $S_{1/2}$	
	Al speciation/complexation		pK values for several Al	
	Aquatic chemistry		reactions	
			parameters for aquatic chemistry	

4.1 The VSD model

The basic equations presented in Chapter 3 have been used to construct a **V**ery **S**imple **D**ynamic (VSD) soil acidification model. The VSD model can be viewed as the simplest extension of the SMB model for critical loads. It only includes cation exchange and N immobilisation, and a mass balance for cations and nitrogen as described above, in addition to the equations included in the SMB model. It resembles the model presented by Reuss (1980) which, however, does not consider nitrogen processes.

In the VSD model, the various ecosystem processes have been limited to a few key processes. Processes that are *not* taken into account, are: (i) canopy interactions, (ii) nutrient cycling processes, (iii) N fixation and NH_4 adsorption, (iv) interactions (adsorption, uptake, immobilisation and reduction) of SO_4, (v) formation and protonation of organic anions, (RCOO) and (vi) complexation of Al with OH, SO_4 and RCOO.

The VSD model consists of a set of mass balance equations, describing the soil input-output relationships, and a set of equations describing the rate-limited and equilibrium soil processes, as described in Section 3. The soil solution chemistry in VSD depends solely on the net element input from the atmosphere (deposition minus net uptake minus net immobilisation) and the geochemical interaction in the soil (CO_2 equilibria, weathering of carbonates and silicates, and cation exchange). Soil interactions are described by simple rate-limited (zero-order) reactions (e.g. uptake and silicate weathering) or by equilibrium reactions (e.g. cation exchange). It models the exchange of Al, H and Ca+Mg+K with Gaines-Thomas or Gapon equations. Solute transport is described by assuming complete mixing of the element input within one homogeneous soil compartment with a constant density and a fixed depth. Since VSD is a single layer soil model neglecting vertical heterogeneity, it predicts the concentration of the soil water leaving this layer (mostly the rootzone). The annual water flux percolating from this layer is taken equal to the annual precipitation excess. The time step of the model is one year, i.e. seasonal variations are not considered. A detailed description of the VSD model can be found in Posch and Reinds (2003).

4.2 The SMART model

The SMART model (**S**imulation **M**odel for **A**cidification's **R**egional **T**rends) is similar to the VSD model, but somewhat extended and is described in De Vries et al. (1989) and Posch et al. (1993). As with the VSD model, the SMART model consists of a set of mass balance equations, describing the soil input-output relationships, and a set of equations describing the rate-limited and equilibrium soil processes. It includes most of the assumptions and simplifications given for the VSD model; and justifications for them can be found in De Vries et al. (1989). SMART models the exchange of Al, H and divalent base cations using Gaines-

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Thomas equations. Additionally, sulphate adsorption is modelled using a Langmuir equation (as in MAGIC) and organic acids can be described as mono-, di- or tri-protic. Furthermore, it does include a balance for carbonate and Al, thus allowing the calculation from calcareous soils to completely acidified soils that do not have an Al buffer left. In this respect, SMART is based on the concept of buffer ranges expounded by Ulrich (1981). Recently a description of the complexation of aluminium with organic acids has been included. The SMART model has been developed with regional applications in mind, and an early example of an application to Europe can be found in De Vries et al. (1994).

4.3   The SAFE model

The SAFE (**S**oil **A**cidification in **F**orest **E**cosystems) model has been developed at the University of Lund (Warfvinge et al. 1993) and a recent description of the model can be found in Alveteg (1998) and Alveteg and Sverdrup (2002). The main differences to the SMART and MAGIC models are: (a) weathering of base cations is not a model input, but it is modelled with the PROFILE (sub-)model, using soil mineralogy as input (Warfvinge and Sverdrup 1992); (b) SAFE is oriented to soil profiles in which water is assumed to move vertically through several soil layers (usually 4), (c) Cation exchange between Al, H and (divalent) base cations is modelled with Gapon exchange reactions, and the exchange between soil matrix and the soil solution is diffusion limited. The standard version of SAFE does not include sulphate adsorption although a version, in which sulphate adsorption is dependent on sulphate concentration and pH has recently been developed (Martinson et al. 2003).

The SAFE model has been applied to many sites and more recently also regional applications have been carried out for Sweden (Alveteg and Sverdrup 2002) and Switzerland (SAEFL 1998, Kurz et al. 1998, Alveteg et al. 1998b).

4.4   The MAGIC model

MAGIC (**M**odel of **A**cidification of **G**roundwater **I**n **C**atchments) is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on soils and surface water chemistry (Cosby et al. 1985a,b,c, 1986). The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in lakes and streams. MAGIC represents the catchment with aggregated, uniform soil compartments (one or two) and a surface water compartment that can be either a lake or a stream. MAGIC consists of (1) a section in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving sulphate adsorption, cation exchange, dissolution-precipitation-speciation of aluminium and dissolution-speciation of inorganic and organic carbon, and (2) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering inputs, net uptake in biomass and losses to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change in surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils.

The soil layers can be arranged vertically or horizontally to represent important vertical or horizontal flowpaths through the soils. If a lake is simulated, seasonal stratification of the lake can be implemented. Time steps are monthly or yearly. Time series inputs to the model include annual or monthly estimates of: (1) deposition (wet plus dry) of ions from the atmosphere; (2) discharge volumes and flow routing within the catchment; (3) biological production, removal and transformation of ions; (4) internal sources and sinks of ions from weathering or precipitation reactions; and (5) climate data. Constant parameters in the model include physical and chemical characteristics of the soils and surface waters, and thermodynamic constants. The model is calibrated using observed values of surface water and soil chemistry for a specified period.

MAGIC has been modified and extended several times from the original version of 1984. In particular organic acids have been added to the model (version 5; Cosby et al. 1995) and most recently nitrogen processes have been added (version 7; Cosby et al. 2001).

The MAGIC model has been extensively applied and tested over a 15-year period at many sites and in many regions around the world. Overall, the model has proven to be robust, reliable and useful in a variety of scientific and managerial activities.

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5 Input Data and Model Calibration

Running a model is usually the least time- and resource-consuming step of an assessment. It takes more time to interpret model output, but most time-consuming is the acquisition of data. Rarely can laboratory or literature data be directly used as model inputs. They have to be pre-processed and interpreted, often with the help of other models. Especially in regional applications not all model inputs are available (or directly usable) from measurements at sites, and interpolations and transfer functions have to be used to obtain the necessary input data. When acquiring data from different sources of information, it is important to keep a detailed record of the 'pedigree', i.e. the entire chain of information, assumptions and (mental) models used to produce a certain number. If possible, also the uncertainty ranges of the data should be estimated and recorded.

Also, when aiming at model runs representing not a single site, but a larger area, e.g. a forest instead of a single tree stand, certain variables ought to be 'smoothed' to represent that larger area. For example, (projected) growth uptake of nutrients (base cations and nitrogen) should reflect the (projected) average uptake of the forest over that area, and not the succession of harvest and re-growth at a particular site. This is also in line with the recommendations made for calculating critical loads with the SMB model (see Mapping Manual).

During the data acquisition the overall goal of the work under the LRTAP Convention should be kept in mind: to support policy decisions on a large regional (European) scale. If best-quality data are not available, we must try to use data that *are* available, and communicate the assumptions and uncertainties involved.

5.1 Input data

The input data needed to run dynamic models depend on the model, but essentially all of them need the following (minimum) data, which can be roughly grouped into in- and output fluxes, and soil properties. Note that this grouping of the input data depends on the model considered. For example, weathering has to be specified as a (constant) input flux in the SMART and MAGIC model, whereas in the SAFE model it is internally computed from soil properties and depends on the state of the soil (e.g. the pH). In- and output fluxes are also needed in the SMB model and are described in detail in the Mapping Manual. This is also true for basic data needed in the SMB model. This chapter thus focuses on additional soil data needed to run dynamic models. The most important soil parameters are the cation exchange capacity (CEC) and base saturation and the exchange (or selectivity) constants describing cation exchange, as well as parameters describing sulphate ad/desorption, since these parameters determine the long-term behaviour (recovery) of soils.

Ideally, all input data are derived from measurements at the site that is modelled. This is usually not feasible for regional applications, in which case input data have to be derived from relationships (transfer functions) with basic (map or GIS) information. In this chapter we provide information on the derivation of input data needed for running the VSD model and thus, by extension, also the other models. Detailed descriptions of the input data for those models can be found in De Vries et al. (1994) for the SMART model, in Cosby et al. (1985a) for the MAGIC model and in Alveteg and Sverdrup (2002) for the SAFE model.

In most of the (pedo-)transfer functions presented in this Chapter, soils, or rather soil groups, are characterised by simple properties: organic carbon and the clay content of the mineral soil. The organic carbon content, C_{org}, can be estimated as 0.5 or 0.4 times the organic matter content in the humus or mineral soil layer, resp. If $C_{org}>15\%$, a soil is considered a *peat* soil. Mineral soils are called *sand* (or sandy soil) in this document, if the clay content is below 18% (coarse textured soils; see table 5), otherwise it is called a *clay* (or clayey/loamy soil). Loess soils are soils with more than 50% silt.
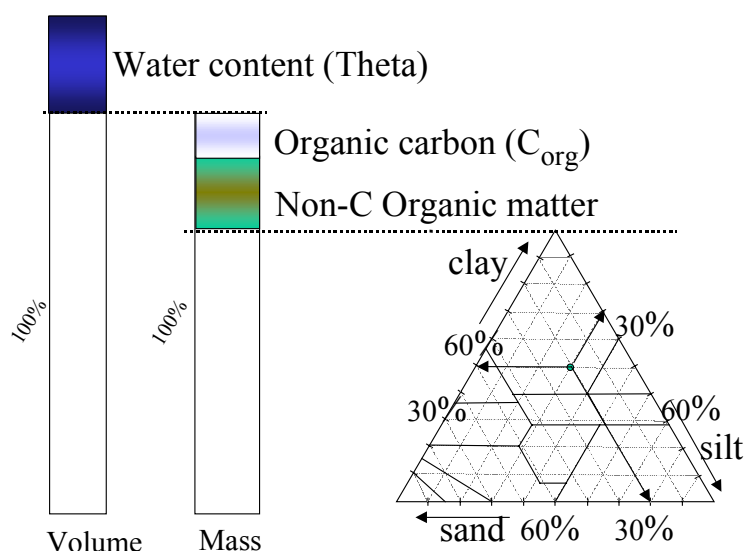
Figure 5: Illustration of the basic composition of a soil profile: soil water, organic matter (organic carbon) and the mineral soil, characterised by its clay, silt and sand fraction (clay+silt+sand=100%)

5.1.1   Input data, as used in critical load calculations

Data that are needed by all mentioned models (VSD, SMART, MAGIC and SAFE) are the inputs and outputs to the soil system, that are also needed in the steady-state SMB model for calculating critical loads. Inputs and outputs to the soil system include atmospheric deposition of base cations, net uptake of nutrients, precipitation and evapotranspiration. Multi-layer models (such as SAFE) also include canopy interactions and organic inputs by litterfall and root decay. These inputs and outputs are either derived from (local) measurements or can be derived by relationships (transfer functions) with basic land/soil and climate characteristics, such as tree species, soil type, elevation, precipitation, temperature etc., which are often available in geographic information systems. More information on this is given in Sverdrup et al. (1990), De Vries (1991) and in Mapping Manual (UBA 1996). Below we elaborate a bit more on deposition data and uptake data, considering their dynamics.

Deposition data:
Scenarios for future sulphur and nitrogen deposition should be provided by integrated assessment modellers, based on atmospheric transport modelling by EMEP. Also future base cation and chloride deposition is needed. At present there are no projections available for these elements on a European scale. Thus in most model applications (average) present base cation depositions are assumed to hold also in the future (and past).

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For a forest soil, actual deposition depends on the type and age of trees (via the 'filtering' of deposition by the canopy). Thus, a tree/forest growth model is needed to compute (local) deposition over time. There is no need for a full-blown growth model here, but one can make use of available information in yield tables, giving data on the evolution of tree height and tree volume over time for given combinations of tree species and site conditions (see below). In any case, a local deposition (adjustment) model should ideally be linked to the dynamic soil model. An example of such a model is the MAKEDEP model, which is part of the SAFE model system (Alveteg and Sverdrup 2002).

Uptake data:

Forest growth influences nutrient uptake, which in turn influences soil (solution) chemistry. In dynamic models, it is not realistic to use steady-state values for growth uptake as it is done in critical load calculations. Instead, many dynamic models describe these processes as a function of actual and projected forest growth. To do so, additional information (forest growth rates for nutrient uptake, etc.) is needed. The amount of data needed in this category depends largely on whether the full nutrient cycle is modelled or whether only net sources and sinks are considered.

Considering net removal by forest growth, as in the VSD, SMART and MAGIC model, the yield (forest growth) at a certain age can be derived from yield tables for the considered tree species. Assuming that the average yield during the rotation period, used in critical load calculations, was derived from such yield tables, the development of the forest during the rotation time can be derived from them and those data are then used as input data for the model. The element contents in stem (and possibly branch) wood should be taken from those used in the critical load calculations.

If the full nutrient cycle is modelled, as in the SAFE model and also an extended version of the SMART model (SMART2, Kros et al. 1995), input data are needed on litterfall rates, root turnover rates, including the nutrient contents in litter (leaves/needles falling from the tree), and fine roots. Such data are highly dependent on tree species and site conditions. Examples of such data for various countries or combinations of tree species and site conditions have been given by De Vries et al. (1990).

Water fluxes:

Water flux data that are needed in the mentioned one-layer models VSD, SMART and MAGIC are limited to the annual precipitation excess leaving the root zone, whereas the multi-layer model SAFE requires water fluxes for each considered soil layer up to the bottom of the root zone. The water flux could be calculated by a separate hydrological model running on a daily or monthly time step, with aggregation to annual values afterwards. Examples of such models are the SWATRE model, which runs with a daily time-step and uses a Darcy approach for modelling soil water movement (De Vries et al. 2001), and WATBAL, which is a capacity-type water balance model running on a monthly time step (Starr 1999). Although the Darcy-type models are scientifically more 'correct', their data needs are large and include daily meteorological data for five meteorological variables (precipitation, temperature, wind speed, radiation and relative humidity) as well as daily throughfall data. Therefore, WATBAL seems more appropriate for regional application.

WATBAL is a monthly water balance model for forested stands/plots, which calculates the components of the water balance equation:

$$PE = P - ET \pm \Delta SM$$

where: PE = precipitation excess, P = precipitation, ET= evapotranspiration and $\pm\Delta SM$ = changes in soil moisture storage. All units are in mm of water and the time interval is monthly. It uses relatively simple input data, which is either directly available (e.g. monthly precipitation and air temperature) or which can be derived from other data using transfer functions (e.g. soil available water capacity, AWC). All the components of the water balance are determined (potential and actual evapotranspiration (PET and AET, respectively), soil moisture (SM) and changes in soil moisture storage, snow store, surface runoff during snowmelt) as well as direct and diffuse radiation.

If national data are not available, the annual water flux through the soil can be derived from meteorological data available on a 0.5°longitude×0.5°latitude grid described by Leemans and Cramer (1991), who interpolated selected records of monthly meteorological data from 1678 European meteorological stations for the period 1931-1960. Actual evapotranspiration is calculated with a model, which is also used in the IMAGE global change model (Leemans and van den Born 1994) following the approach by Prentice et al. (1993).

5.1.2   Soil data, as used in critical load calculations

Input to the SMB model, and thus also to all dynamic soil acidification models includes also basic soil data, such as weathering rates, N transformation rates, specifically (de)nitrification, and equilibrium constants for Al dissolution and CO_2 dissociation. A summary of information on those variables is given below.

Weathering rates:
There are various possibilities to assess weathering rates including (see Sverdrup et al. 1990, and Mapping Manual):
- Estimation of the depletion of base cations in the soil profile by: (i) chemical analyses of different soil horizons including the parent material (average weathering rate over the period of soil formation) or (ii) input output budgets based on hydrochemical monitoring (current weathering rate).
- Correlation between the weathering rate and the total base cation content (Olsson and Melkerud 1991).
- Weathering models, such as PROFILE to estimate field weathering rates based on the soil mineralogy (Sverdrup 1990).
- Assignment of a weathering rate to European forest soils based on the parent material and texture class of a given (dominant) soil unit (De Vries 1991 and Mapping Manual).

At present, PROFILE is most frequently used when detailed data on soil mineralogy (total analyses) are available, and the simple assignment to forest soils when such data are not available. For more information, refer to the respective references.

Rate constants or fractions for mineralisation and (de-)nitrification:
Rate constants for mineralisation, nitrification and denitrification are needed in detailed models such as SAFE. For those data we refer to relevant publications. Simple models mostly use factors between zero and one, which compute nitrification and denitrification as fraction of the (net) input of N.

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As with the SMB model, in the VSD model complete nitrification is assumed (nitrification fraction equals 1.0). For the complete soil profile, the nitrification fraction in forest soils varies mostly between 0.75 and 1.0. This is based on NH_4/NO_3 ratios below the rootzone of highly acidic Dutch forests with very high NH_4 inputs in the early nineties, which were nearly always less than 0.25 (De Vries et al. 1995). Generally, 50% of the NH_4 input is nitrified above the mineral soil in the humus layer (Tietema et al. 1990). Actually, the nitrification fraction includes the effect of both nitrification and preferential ammonium uptake.

Denitrification fractions, which are used in the SMB, VSD and SMART model can be related to soil type as suggested in Table 3. Ranges are based on data given by Steenvoorden (1984) and Breeuwsma et al. (1991) for peat, clay and sandy soils in the Netherlands. In deeply drained sandy forest soils, denitrification appears to be nearly negligible (Klemedtson and Svensson 1988).

Table 3: *Ranges in denitrification fractions for different soil types.*

Soil type	Denitrification fraction (-)
Peat	0.80-0.95
Clay	0.7-0.8
Sandy/ Loess soils:	
- with gleyic features	0.4-0.6
- without gleyic features	0.0-0.2

Al equilibrium constant and exponent:
As in the SMB and SAFE model, Al dissolution is often described by a gibbsite equilibrium. Values for $\log_{10}K_{gibb}$ generally vary between 8.0 and 8.5. In general the Al concentration depends upon the H concentration and a site dependent exponent, as given in eq.3.8. This description is, e.g. used in the VSD, SMART and MAGIC model. Values for KAl_{ox} and the exponent a depend on the soil depth.

Especially in forest topsoils, it is more accurate to use values for a that are lower than 3, and consequently also a different $\log K$ value. Regression analyses between the negative logarithm of the Al concentration (pAl) against the negative logarithm of the H concentration (pH), with concentrations in mol.l^{-1} for nearly 300 Dutch forest stands give results as presented in Table 4. The data are based on measurements in approximately 200 sandy soils (Leeters and de Vries 2001) and in approximately 40 loess soils, 30 clay soils and 30 and peat soils (Klap et al. 1999). The results show that the standard gibbsite equilibrium constant and exponent of 3.0 is reasonable for clay soils. Very different values, however, are required for peat soils and to a lesser extent also for sandy and loess soils, especially at lower soil depths (relevant for multi-layer models such as SAFE).

Table 4: Estimated values of KAl$_{ox}$ and the exponent a based on regression between pAl and pH in the solution of Dutch soils (Van der Salm and De Vries 2001).

Soil type	Depth (cm)	log KAl_{ox}	a	R^2_{adj}	n
Sandy soils	0-10	-0.56	1.17	56.1	195
	10-30	2.37	1.88	82.8	348
	30-100	5.20	2.51	86.3	172
Peat	all depths	-1.06	1.31	81.2	116
Clay	all depths	7.88	2.65	87.3	116
Loess	0- 10	-0.48	1.06	64.1	39
	10- 30	3.29	1.90	87.9	39
	30-100	4.55	2.17	92.4	39

Formulae for converting chemical equilibrium constants, such as KAl_{ox}, to other units, e.g. from mol/l to eq/m^3, can be found in Annex C.

5.1.3 Data needed to simulate cation exchange

In all models, cation exchange is a crucial process. For the VSD model it is the only process included in addition to the SMB model. Data needed to allow exchange calculations are:

- The pool of exchangeable cations, being the product of layer thickness, bulk density, cation exchange capacity (CEC) and exchangeable cation fractions
- Cation exchange constants (selectivity coefficients)

Preferably these data are taken from measurements. Such measurements generally made for several soil horizons. For single-layer models, such as VSD, such data have to be properly averaged over the entire soil depth (rooting zone). Formulae for carrying out these averaging are provided in Annex D.

In the absence of measurements, the various data needed to derive the pool of exchangeable cations for major forest soil types can be derived by extrapolation of point data, by using transfer functions between bulk density, CEC and base saturation and basic land and soil characteristics, such as soil type, soil horizon, organic matter content, soil texture, etc. (De Vries 1991). An overview of such transfer functions and data on soil variables, soil properties and soil constants is given below. If new data are to be obtained, various approaches and analyses methods can be used. This is discussed in Annex E.

Soil bulk density:
If no measurements of soil bulk density are available, it can be computed from the following transfer function:

$$(5.1) \qquad \rho = \begin{cases} 1/(0.625 + 0.05 \cdot C_{org} + 0.0015 \cdot clay) & \text{for} & C_{org} \leq 5\% \\ 1.55 - 0.0814 \cdot C_{org} & \text{for} & 5\% < C_{org} < 15\% \\ 0.725 - 0.337 \cdot \log_{10} C_{org} & \text{for} & C_{org} \geq 15\% \end{cases}$$

where ρ is the bulk density (g cm^{-3}), C_{org} is the organic carbon content and *clay* the clay content (both in %). The top equation for mineral soils is based on data by Hoekstra and Poelman (1982), the bottom equation for peat(y) soils is derived from Van Wallenburg (1988) and the central equation is a linear interpolation (for *clay*=0) between the two (Reinds et al. 2001).

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Cation exchange capacity (CEC):

The value of the CEC depends on the soil pH at which the measurements are made. Consequently, there is a difference between unbuffered CEC values, measured at the actual soil pH and buffered values measured at a standard pH, such as 6.5 or 8.2 (see Annex E). In the VSD (and many other) models the exchange constants are related to a CEC that is measured in a buffered solution in order to standardise to a single pH value (e.g., pH=6.5, as upper limit of non-calcareous soils). The actual CEC can be calculated from pH, clay and organic carbon content according to (after Helling et al. 1964):

$$(5.2) \qquad CEC(pH) = (0.44 \cdot pH + 3.0) \cdot clay + (5.1 \cdot pH - 5.9) \cdot C_{org}$$

where CEC is the cation exchange capacity (meq/kg), $clay$ is the clay content (%) and C_{org} the organic carbon content (%). The pH in this equation should be as close as possible to the measured soil solution pH. The clay content can be derived from national soil information systems or related to the texture class. For sandy soils the clay content can be set to zero in eq.5.2. The organic carbon content of the various soil types can also be derived from these sources. Values range from 0.1% for arenosols (Qc) to 50% for peat soils (Od). Typical average clay contents as function of the texture class, presented on the FAO soil map, are given in Table 5.

Table5: *Typical average clay contents and base saturation as a function of soil texture classes.*

Texture class	Name	Definition	Clay content (%)	Base saturation (%)
1	coarse	clay < 18% and sand ≥ 65%	6	5
2	medium	clay < 35% and sand ≥ 15%; but clay ≥ 18% if sand ≥ 65%	20	15
3	medium fine	clay < 35% and sand < 15%	20	20
4	fine	35% ≤ clay < 60%	45	50
5	very fine	clay ≥ 60%	75	50
9	organic soils	Soil types O	5	10-70

Computing $CEC(pH_{measured})$, i.e. the CEC from eq.5.2, using measured (site-specific) C_{org}, $clay$ and pH does not always match the measured CEC, $CEC_{measured}$, and thus computing CEC at pH=6.5, $CEC(6.5)$, would not be consistent with it. Nevertheless, eq.5.2 can be used to *scale* the measured CEC to a value at pH=6.5, i.e. the value needed for modelling, in the following manner:

$$(5.3) \qquad CEC_{pH=6.5} = CEC_{measured} \cdot \frac{CEC(6.5)}{CEC(pH_{measured})}$$

This method of scaling measured data with the ratio (or difference) of model output is widely used in global change work to obtain, e.g., climate-changed (meteorological) data consistent with observations.

Exchangeable base cation fraction (base saturation):

In most models, a lumped expression is used for the exchange of cations, distinguishing only between H, Al and base cations (VSD, SMART and SAFE). As with the clay content, data for the exchangeable cation fractions, or in some cases only the base saturation, can be based on information on national soil information systems, or in absence of these, on the FAO soil map of Europe (FAO 1981). Base saturation data vary from 5-25% in relatively

acid forest soils to more than 50% in well buffered soils. A very crude indication of the base saturation as a function of the texture class of soils is given in the last column of Table 5. The relationship in Table 5 is based on data from forest soils given in FAO (1981) and in Gardiner (1987). A higher texture class reflects a higher clay content implying an increase in weathering rate, which implies a higher base saturation. For organic soils the initial base saturation is put equal to 70% for eutric histosols (Oe) and 10% for dystric histosols (Od).

The most preferred method is to use measured CEC and exchangeable cation data. For a national application, such data are, however, often lacking. When data on the initial base saturation of soils are not available for regional (national) model applications, one may derive them from a relationship with environmental factors. Such an exercise was carried out using a European database with approximately 5300 soil chemistry data for the organic layer and the forest topsoil (0-20 cm) collected on a systematic 16x16 km^2 grid (ICP Forest level-I grid; Vanmechelen et al. 1997). The regression relationship for the estimated base saturation E_{BC} (expressed as a fraction with values between 0 and 1) is:

$$
\ln\left(\frac{E_{BC}}{1 - E_{BC}}\right) = a_0 + a_1(\text{soil group}) + a_2(\text{tree species}) + a_3 \cdot \text{altitude} + a_4 \cdot \ln(\text{age})
$$

$$
(5.4) \qquad + a_5 \cdot \text{temperature} + a_6 \cdot (\text{temperature})^2 + a_7 \cdot \ln(\text{precipitation})
$$

$$
+ \sum_{k=8}^{11} a_k \cdot \ln(\text{deposition}_k) + \sum_{k=12}^{15} a_k \cdot \text{lt}(\text{deposition fraction}_k)
$$

where 'ln' is the natural logarithm, lt(x)=ln(x/(1-x)), and the a_k's are the regression coefficients. The regression analysis was carried out using a so-called Select-procedure. This procedure combines qualitative predictor variables, such as tree species and/or soil type, with quantitative variables and it combines forward selection, starting with a model including one predictor variable, and backward elimination, starting with a model including all predictor variables. The 'best' model was based on a combination of the percentage of explained variance, that should be high and the number of predictor variables that should be low.

In the analyses the soils were grouped in ten major FAO soil types (De Vries et al. 1998) but for this analysis, they were further clustered to four major categories, namely sandy soils, loam/clay soils, peat soils and calcareous soils (not shown here). Results are limited to four major tree species, pine, spruce, oak and beech, which predominate in Northern and Central Europe. Data on temperature and precipitation are based on interpolations from meteorological stations for a 10-year period (1985-1996), as an approximation of average meteorological conditions. Atmospheric deposition data were derived from EDACS model calculations. More information on the procedure is given in Klap et al. (2002). Results of the analyses are given in Table 6. The explained variance for base saturation was approx. 45%.

Note: When data are not available, one may also calculate base saturation as the maximum of (i) a relation with environmental factors as given above and (ii) an equilibrium with present deposition levels of SO_4, NO_3, NH_4 and BC. Especially in southern Europe, where acid deposition is relatively low and base cation input is high, the base saturation in equilibrium with the present load can be higher than the value computed according to Table 6.

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Table 6: Coefficients for estimating base saturation and the C/N-ratio in the mineral topsoil (0-20cm) and the organic layer (after Klap et al. 2002).

Predictor variable	Base saturation (mineral topsoil)	C/N-ratio organic layer	C/N-ratio mineral topsoil	Coefficients in eqs.(5.4) and (5.6)
Constant	3.198	3.115	1.310	a_0
Soil group:				
Sandy soils	0	0	0	a_1
Loamy/clayey soils	0.297	-0.807	-0.279	a_1
Peat soils	0.534	-0.025	-0.312	a_1
Tree species:				
Pine	0	0	0	a_2
Spruce	-0.113	-0.158	-0.093	a_2
Oak	0.856	-0.265	-0.218	a_2
Beech	0.591	-0.301	-0.218	a_2
Site conditions:				
Altitude [m]	-0.00014	-0.00008	-0.000136	a_3
Age [yr]	0	0.025	0.096	a_4
Meteorology:				
Temperature [°C]	0	-0.0078	-0.041	a_5
Temperature^2 [°C^2]	0	0.00095	0.0014	a_6
Precipitation [mm/yr]	0	0.178	0.194	a_7
Deposition:				
Na [eq/ha/yr]	-0.223	0	0.080	a_8
N-tot (=NO$_y$+NH$_z$) [eq/ha/yr]:				
Sandy soils	0	-0.150	-0.019	a_9
Loamy/clayey soils	0	-0.032	0	a_9
Peat soils	0	-0.136	0	a_9
Acid (=SO$_x$-ssc[a] + N-tot) [eq/ha/yr]	-1.025	0	0	a_{10}
Bc-ssc[a] (=Ca+Mg+K-ssc) [eq/ha/yr]	0.676	0	0	a_{11}
Deposition fractions:				
NH$_z$ / Acid [-]:				
Sandy soils	0	0	0	a_{12}
Loamy/clayey soils	-0.494	0	0	a_{12}
Peat soils	-0.896	0	0	a_{12}
NH$_z$ / N-tot [-]	0	0.102	0.120	a_{13}
Ca-ssc[a] / Bc-ssc [-]	1.211	0	0	a_{14}
Mg-ssc[a] / Bc-ssc [-]	0.567	0	0	a_{15}

[a] ssc = sea salt corrected; if <0.1, set =0.1 to avoid underflow in the equations.

Other exchangeable cation fractions:

Separate exchangeable base cation fractions (as needed in the MAGIC model) could not be derived from environmental factors, as described above, since data were not available. The same holds for Al, which is a crucially important exchangeable cation. Thus a relationship was derived between the exchangeable Al fraction, E_{Al}, and the base saturation, E_{Bc}, based on data in the sandy, loess and clay soils described above (De Vries and Leeters 2001, Leeters and De Vries 2001, Klap et al. 1999). The fitted relationship is:

$$(5.5) \qquad E_{Al} = A + \frac{C}{1 + \exp(-B(E_{Bc} - M))}$$

with the coefficients given in Table 7.

Table 7: *Coefficients describing the relationship between exchangeable Al fraction and base saturation.*

Soil group	A	C	B	M	R^2-adj (%)
Sand	0.01236	17.73	-5.117	-0.7562	59
Loess	-0.07161	37.32	-2.877	-1.385	82
Clay	0.00031	0.22731	-13.65	0.33769	86
All soils	-0.0028	0.4414	-7.54	0.2194	63

Exchange constants:

In most exchange models the cations are lumped to H, Al and base cations (VSD, SMART and SAFE), but in MAGIC every base cation (Ca, Mg, K, Na) is modelled separately. Furthermore, cation exchange in SMART and MAGIC is based upon Gaines-Thomas equations, in SAFE it is described by Gapon exchange reactions, whereas in the VSD model the user can chose between the two. Exchange constants can be derived from the simultaneous measurement of the major cations (H, Al, Ca, Mg, K and Na) on the adsorption complex and in the soil solution.

Decadic logarithms of average exchange constants thus derived for sand, loess, clay and peat soils with their standard deviations ('stddev'), are given in the Tables below. As with the Al dissolution data, the data are based on measurements in approximately 200 sandy soils (Leeters and De Vries 2001) and in approximately 40 loess soils, 30 clay soils and 30 and peat soils (Klap et al. 1999). The tables show the high affinity of the complex for protons compared to all other monovalent cations. The relative contributions of K, Na and NH_4 on the adsorption complex are very low. Formulae for the conversion of units are provided in Annex C. A detailed overview over data sources, calculation methods and connections/correlations between the various exchange constants can be found in De Vries and Posch (2003).

Results for the exchange constants needed in the VSD model (in 'Gaines-Thomas mode') are given in the Tables 8 and 9. The exchange constants needed in this model are only related to the exchange between H and Bc=Ca+Mg+K and between Al and Bc.

Table 8: *Mean and standard deviation of logarithmic **Gaines-Thomas** exchange constants of **H** against **Ca+Mg+K** as a function of soil depth for sand, loess, clay and peat soils $(mol/l)^{-1}$.*

Layer (cm)	Sand		Loess		Clay		Peat	
	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	5.338	0.759	5.322	0.692	6.740	1.464	4.754	0.502
10-30	6.060	0.729	5.434	0.620	6.007	0.740	4.685	0.573
30-60	6.297	0.656	-	-	6.754	0.344	5.307	1.051
60-100	6.204	0.242	5.541	0.579	7.185	-	5.386	1.636
0-30	5.236	0.614	5.386	0.606	6.728	1.373	4.615	0.439
0-60	5.863	0.495	-	-	6.887	1.423	4.651	0.562

*Table 9: Mean and standard deviation of logarithmic **Gaines-Thomas** exchange constants of **Al** against **Ca+Mg+K** as a function of soil depth for sand, loess, clay and peat soils (mol/l).*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	2.269	1.493	1.021	1.147	1.280	1.845	0.835	1.204
10-30	3.914	1.607	1.257	0.939	-0.680	1.152	0.703	0.968
30-60	4.175	1.969	-	-	-3.070	0.298	0.567	1.474
60-100	2.988	0.763	1.652	1.082	-2.860	-	0.969	1.777
0-30	2.306	1.082	0.878	1.079	0.391	1.555	0.978	0.805
0-60	2.858	1.121	-	-	-0.973	1.230	0.666	0.846

Results for the exchange constants needed in the SMART model are given in Tables 10 and 11. The exchange constants needed in this model are related to the exchange between H and Ca+Mg, Al and Ca+Mg.

*Table 10: Mean and standard deviation of logarithmic **Gaines-Thomas** exchange constants of **H** against **Ca+Mg** as a function of soil depth for sand, loess, clay and peat soils $(mol/l)^{-1}$.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	5.200	0.779	5.306	0.704	6.703	1.500	4.573	0.549
10-30	5.968	0.715	5.474	0.587	5.999	0.740	4.579	0.576
30-60	6.249	0.660	-	-	6.734	0.344	5.243	1.042
60-100	6.393	0.249	5.519	0.553	7.155	-	5.343	1.627
0-30	5.136	0.607	5.391	0.590	6.709	1.391	4.487	0.468
0-60	5.739	0.513	-	-	6.876	1.430	4.575	0.583

*Table 11: Mean and standard deviation of logarithmic **Gaines-Thomas** exchange constants of **Al** against **Ca+Mg** as a function of soil depth for sand, loess, clay and peat soils (mol/l).*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean.	stddev	Mean.	stddev	Mean.	stddev	Mean.	stddev
0-10	1.856	1.557	0.974	1.154	1.170	1.781	0.294	1.230
10-30	3.639	1.517	1.376	1.045	-0.703	1.182	0.385	1.016
30-60	4.029	1.853	-	-	-3.128	0.298	0.376	1.542
60-100	3.553	0.899	1.586	1.100	-2.951	-	0.840	1.761
0-30	2.004	1.057	0.892	1.158	0.334	1.521	0.592	0.859
0-60	2.486	1.008	-	-	-1.005	1.252	0.437	0.902

Results for the exchange constants needed in the MAGIC model are given in the Tables 12-15. Note that the exchange of protons against Al or base cations is not included in the MAGIC model. It should be noted, however, that in the MAGIC model *activities* are used instead of concentrations. In an earlier version of MAGIC (Cosby et al. 1985) another, but equivalent, set of exchange equations had been used.

*Table 12: Mean and standard deviation of logarithmic **Gaines-Thomas** exchange constants of **Al** against **Ca** as a function of soil depth for sand, loess, clay and peat soils (mol/l).*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	1.630	1.581	0.931	1.194	1.080	1.814	0.072	1.242
10-30	3.287	1.542	1.395	1.122	-0.812	1.216	0.197	0.998
30-60	3.654	2.100	-	-	-3.253	0.432	0.154	1.527
60-100	3.545	1.084	1.677	1.179	-3.329	-	0.560	1.742
0-30	1.719	1.058	0.860	1.193	0.206	1.515	0.392	0.840
0-60	2.010	1.094	-	-	-1.125	1.292	0.216	0.886

*Table 13: Mean and standard deviation of logarithmic **Gaines-Thomas** exchange constants of **Al** against **Mg** as a function of soil depth for sand, loess, clay and peat soils (mol/l).*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	2.346	1.637	1.116	1.071	1.478	1.727	0.805	1.403
10-30	3.995	1.588	1.373	0.965	-0.391	1.116	0.935	1.249
30-60	4.378	1.791	-	-	-2.841	0.022	1.010	1.742
60-100	3.583	0.670	1.509	1.032	-1.866	-	1.340	1.976
0-30	2.554	1.008	1.022	1.091	0.783	1.573	1.131	1.070
0-60	3.142	1.031	-	-	-0.594	1.195	1.024	1.154

*Table 14: Mean and standard deviation of logarithmic **Gaines-Thomas** exchange constants of **Al** against **K** as a function of soil depth for sand, loess, clay and peat soils $(mol/l)^2$.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	-1.065	1.086	-2.637	1.032	-2.931	1.664	-1.228	0.977
10-30	-0.398	1.144	-2.498	0.972	-4.288	0.749	-0.944	0.578
30-60	-0.676	1.494	-	-	-5.162	0.319	-0.887	0.940
60-100	-2.670	0.880	-1.715	0.912	-4.653	-	-0.639	1.349
0-30	-0.876	0.816	-2.678	0.848	-3.539	1.548	-0.888	0.505
0-60	-0.838	0.868	-	-	-4.426	0.706	-0.910	0.522

*Table 15: Mean and standard deviation of logarithmic **Gaines-Thomas** exchange constants of **Al** against **Na** as a function of soil depth for sand, loess, clay and peat soils $(mol/l)^2$.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	1.268	1.170	1.783	1.016	1.338	0.925	0.822	0.958
10-30	2.496	1.313	0.335	1.568	0.107	0.633	0.836	0.604
30-60	2.310	1.500	-	-	-0.538	0.053	0.922	0.891
60-100	1.064	0.374	-0.796	1.301	0.024	-	0.879	1.060
0-30	1.977	0.827	0.996	1.287	1.264	0.942	1.089	0.592
0-60	2.181	0.819	-	-	0.732	0.787	0.944	0.569

Finally, the Gapon exchange constants for the cations used in VSD (in 'Gapon mode') and SAFE are given in the Tables 16-17. Beware of the different units of the exchange constants compared to the Gaines-Thomas equations due to a different description of the exchange process (see eqs.3.11-3.14).

*Table 16: Mean and standard deviation of logarithmic **Gapon** exchange constants of **H** against **Ca+Mg+K** as a function of soil depth for sand, loess, clay and peat soils $(mol/l)^{-1/2}$.*

Layer	Sand		Loess		Clay		Peat	
(cm)	Mean	stddev	Mean	stddev	Mean	stddev	Mean	stddev
0-10	3.178	0.309	3.138	0.268	3.684	0.568	2.818	0.199
10-30	3.527	0.271	3.240	0.221	3.287	0.282	2.739	0.175
30-60	3.662	0.334	-	-	3.521	0.212	2.944	0.382
60-100	3.866	0.125	3.232	0.251	3.676	-	3.027	0.672
0-30	3.253	0.311	3.170	0.206	3.620	0.530	2.773	0.190
0-60	3.289	0.340	-	-	3.604	0.654	2.694	0.170

rivm

*Table 17: Mean and standard deviation of logarithmic **Gapon** exchange constants of Al against **Ca+Mg+K** as a function of soil depth for sand, loess, clay and peat soils (mol/l)$^{1/6}$.*

Layer (cm)	Sand Mean	Sand stddev	Loess Mean	Loess stddev	Clay Mean	Clay stddev	Peat Mean	Peat stddev
0-10	0.306	0.440	0.190	0.546	-0.312	0.738	-0.373	0.350
10-30	0.693	0.517	0.382	0.663	-0.463	0.431	-0.444	0.255
30-60	0.819	0.527	-	-	-1.476	0.093	-0.740	0.336
60-100	1.114	0.121	0.390	0.591	-1.795	-	-0.867	0.401
0-30	0.607	0.472	0.221	0.647	-0.609	0.731	-0.247	0.404
0-60	0.199	0.633	-	-	-1.054	0.362	-0.551	0.210

Note that exchange constants are not independent (see eqs. 3.12 and 3.13). For example, the mean of the logarithm of the Gapon exchange constant for H-Al exchange can be obtained by subtracting a value in Table 17 from the respective value in Table 16. These and other formulae relating the different exchange constants can be found in De Vries and Posch (2003).

5.1.4 Data needed to include balances for nitrogen, sulphate and aluminium

C/N-ratio:

As with CEC and base saturation, data for the C/N-ratio of soils should preferably be based on measurements. For national applications, it can also be based on information on national soil information systems, or in absence of this on the FAO soil map of Europe (FAO 1981). Data for the C/N-ratio generally vary between 15 in rich soils where humification has been high to 40 in soils with low N inputs and less humification. Values can also be obtained from results of a regression analysis similar to that of the base saturation according to:

$$
\ln(\text{C/N - ratio}) = a_0 + a_1 (\text{soil group}) + a_2 (\text{tree species}) + a_3 \cdot \text{altitude} + a_4 \cdot \ln(\text{age})
$$

(5.6)
$$
+ a_5 \cdot \text{temperature} + a_6 \cdot (\text{temperature})^2 + a_7 \cdot \ln(\text{precipitation})
$$

$$
+ \sum_{k=8}^{11} a_k \cdot \ln(\text{deposition}_k) + \sum_{k=12}^{15} a_k \cdot \text{lt}(\text{deposition fraction}_k)
$$

where $\text{lt}(x) = \ln(x/(1-x))$. Results of the analysis, which was performed with the same data sets as described in the section on base saturation, are given in Table 6. As with the base saturation, more information on the procedure is given in Klap et al. (2002).

Sorption capacity and half-saturation constant for sulphate:

Values for the maximum sorption capacity for sulphate, S_{max}, can be related to the content of oxalate extractable Al (meq kg^{-1}) according to (Johnson and Todd 1983):

(5.7)
$$
S_{max} = 0.02 \cdot Al_{ox}
$$

Estimates for the oxalate extractable Al content are given below. Adsorption or half-saturation constants for sulphate, $S_{1/2}$, can be derived from literature information (e.g. Singh and Johnson 1986, Foster et al. 1986). A reasonable average value is 1.0 eq/m^3.

Al-hydroxide content:

Data for the oxalate extractable Al content (the content of readily available Al-hydroxide) are available in several national soil information systems, such as the soil information

system of the Netherlands. In sandy soils the Al-hydroxide content (in meq/kg) mostly varies between 100-200 for A-horizons, between 200-350 for B-horizons and between 50-150 for C-horizons (parent material, De Vries 1991).

Moisture content:
In any dynamic model, which includes a mass balance for elements, information on the soil moisture content is needed. An approximation of the annual average soil moisture content can be made as a function of the clay content according to (Brady 1972):

(5.8) $$\theta = 0.04 + 0.0077 \cdot clay$$

This equation holds for clay contents up to 30%. Above 30% a constant value of 0.27 is assumed.

5.2 Model calibration

If all input parameters, initial conditions and driving forces were known, the chosen model would describe the future development of the soil chemical status for any given deposition scenario. However, in most cases several of the parameters are poorly known, and thus many models, i.e. the badly known parameters in the model, have to be 'calibrated'. The method of calibration varies with the model and/or the application.

In standard applications of both the MAGIC and SAFE model it is assumed that in pre-acidification times (say 1850) the input of ions is in equilibrium (steady state) with the soil (solution) chemistry. Furthermore it is assumed that the deposition history of all (eight) ions is known (properly reconstructed).

In SAFE, weathering rates and uptake/net removal of N and base cations are computed within the model (see above). Only simulated present base saturation is matched with observations (in every soil layer) by adjusting the cation exchange selectivity coefficient(s). Matching simulated and observed soil solution concentrations is not part of the standard calibration procedure.

The calibration of MAGIC is a sequential process whereby firstly the input and output of those ions assumed to act conservatively in the catchment are balanced (usually only Cl). Next, the anion concentrations in surface waters are matched by adjusting catchment net retention (of N) and soil adsorption (of S) if appropriate. Thirdly, the four individual major base cation concentration in the stream and on the soil solid phase (expressed as a percentage of cation exchange capacity) are matched by adjusting the cation exchange selectivity coefficients and the base cation weathering rates. Finally, surface water pH, Al and organic anion concentrations are matched by adjusting the aluminium solubility coefficient and total organic acid concentration in surface water.

Both in MAGIC and SAFE automatic calibration routines are part of the overall model system. For the SMART and VSD model no such automatic model calibration routines are presently available. To date, in site-specific applications calibration has been carried out by 'trial and error', and in European applications the initial base saturation in 1960 has been derived from transfer functions, thus avoiding any calibration and the reconstruction of historic (pre-1960) depositions.

6 Model Calculations and Presentation of Model Results

6.1 Model calculations, especially target loads

For every model, the most demanding part is not the actual running of the model, but the derivation and preparation of input data (files) and the model initialisation/calibration. For regional applications, i.e. runs for many sites, additional work is usually required to embed the model – designed for a single site – into a suitable (data base) framework which allows the efficient handling of model inputs and outputs.

As outlined above (section 2.3), target loads, or target load functions in the case of acidification, are a feasible way to interact with integrated assessment models, not least due to their similarity with critical load functions. The computation of target loads is not straightforward. After specifying the target year and the year of implementation of the (yet unknown) target load, the dynamic model has to be run iteratively, until the deposition (= target load) is found which is required for the soil to reach the desired chemical status in the specified target year. The following examples demonstrate the different cases that can arise when calculating target loads and what can happen when doing such calculation 'blindly'. For simplicity we use a single deposition, but the conclusions hold for target load functions as well.

As an example, Figure 6 shows the deposition history (left) and the resulting molar Al/Bc-ratio (right) as simulated (by the VSD model) for three different soils, characterised by their CEC (40, 60 and 80 meq/kg). In two cases the Al/Bc-ratio at 'present' (year 2010) is above the critical value (=1), while for CEC=80 it stayed below it during the past.
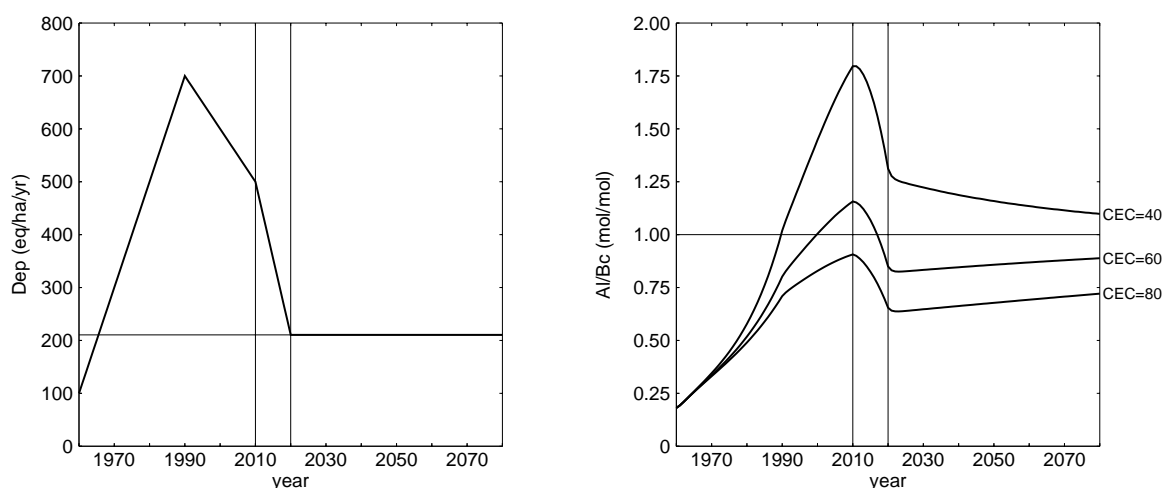

Figure 6: Temporal development of acidifying deposition (left) and corresponding molar Al/Bc-ratio (right) for 3 soils varying in CEC. The two vertical lines separate 50 years of 'history', 10 years (2010-2020) of implementation, and the future. Also shown are the critical load and the critical value $(Al/Bc)_{crit}=1$ as thin horizontal lines. The deposition drops to the critical load within the implementation period and the Al/Bc-ratios (slowly) approach the critical value.

To investigate the future behaviour of the soils, we let the deposition drop to the critical load (which is independent of the CEC) during the 'implementation decade' (marked by two vertical lines in Figure 6). Obviously, for CEC=80, the Al/Bc-ratio stays below one, whereas for CEC=60 it drops below one within the first decade and then slowly rises again towards the critical value. For CEC=40, the Al/Bc-ratio stays well above the critical value, approaching it asymptotically over time. In all three cases the approach to the critical value is very slow.

Next we look at target load calculations for these three soils. Figure 7 shows the results of target load calculations for 40 years, i.e. achieving $(Al/Bc)_{crit}=1$ in the year 2050. For CEC=40 meq/kg the target load is smaller than the critical load, as one would expect. For CEC=60 and 80, however, the computed target loads are higher than the critical load. As Figure 7 illustrates, this does not make sense: After reaching the critical limit, these two soils deteriorate and the Al/Bc-ratio gets larger and larger. Since target loads are supposed to protect also *after* the target year, we stipulate that **whenever a calculated target load is higher than the critical load, it has to be set equal to the critical load.**
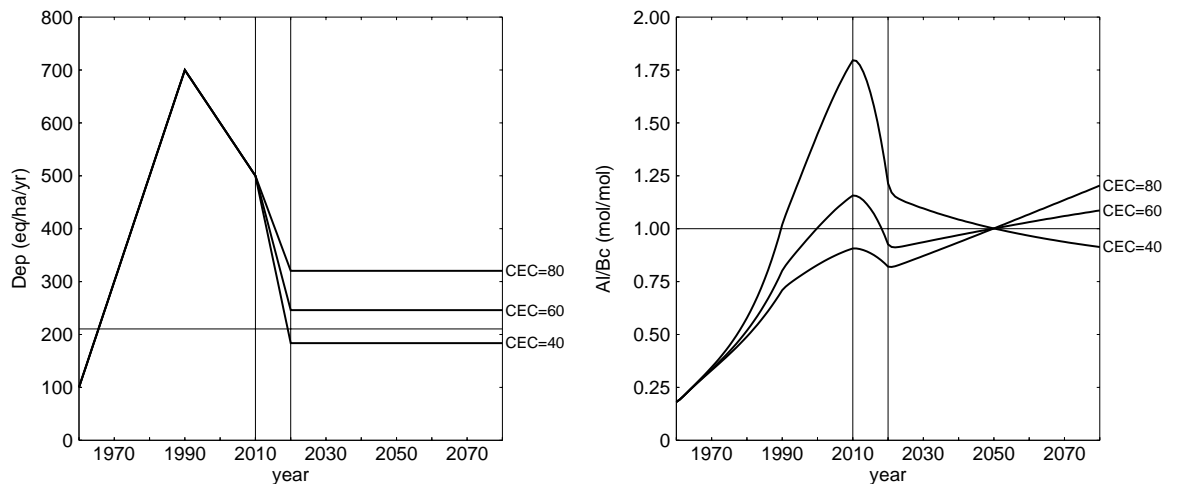

Figure 7: Target loads (with 2050 as target year) for three soils and the resulting Al/Bc-ratio (left). Note that for CEC=60 and 80 the target load is higher than the critical load, even when $(Al/Bc)_{crit}<1$ at present (for CEC=80)! Clearly, in such cases target load calculations don't make sense.

In the light of the above considerations we define that *a target load is the deposition for which a pre-defined chemical or biological status is reached in the target year and maintained (or improved) thereafter.*

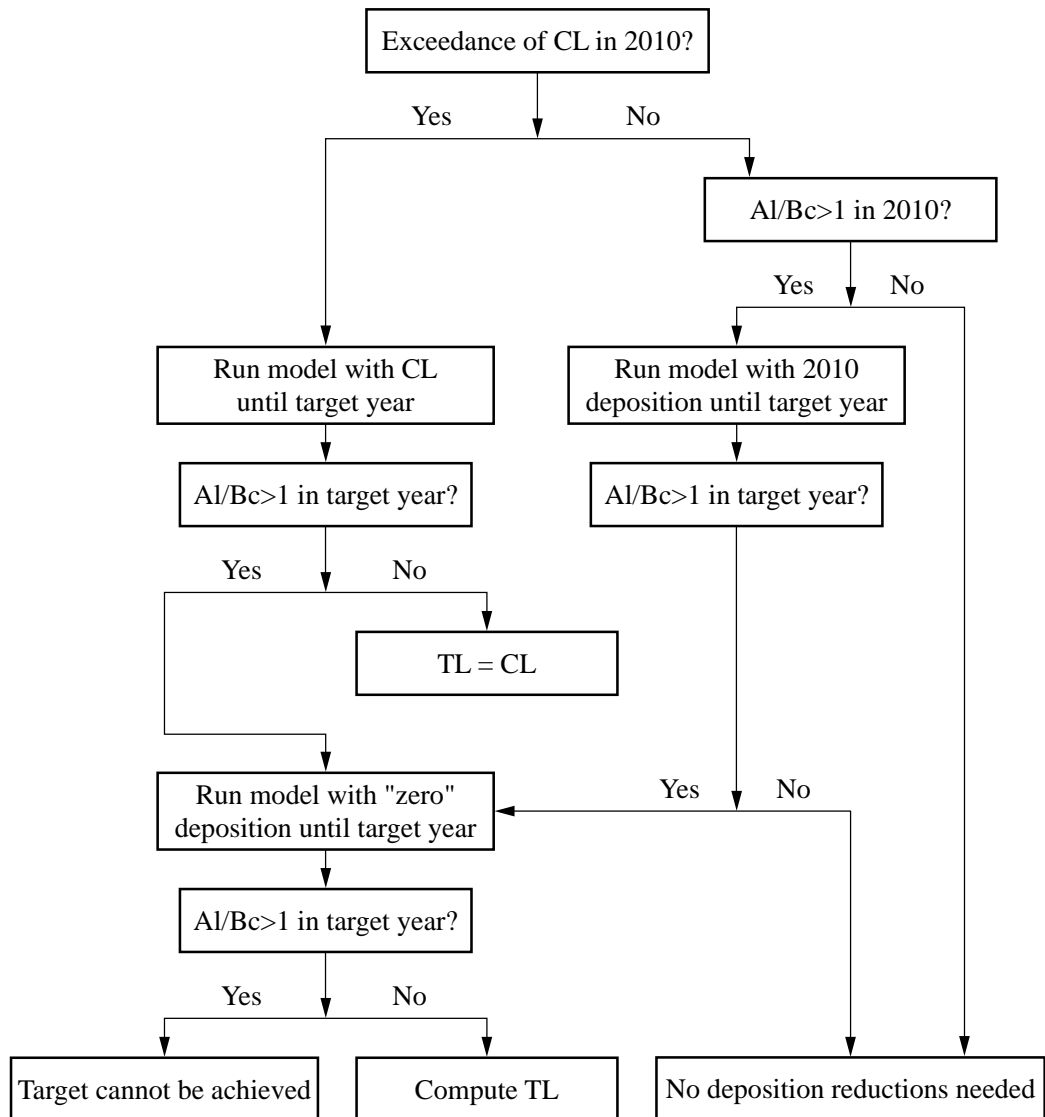In view of this, the calculation of a target load should be carried out as depicted by the flow chart in Figure 8.

Exceedance of CL in 2010?

Yes — No

Al/Bc>1 in 2010?

Yes — No

Run model with CL until target year

Run model with 2010 deposition until target year

Al/Bc>1 in target year?

Al/Bc>1 in target year?

Yes — No

TL = CL

Run model with "zero" deposition until target year

Yes — No

Al/Bc>1 in target year?

Yes — No

Target cannot be achieved

Compute TL

No deposition reductions needed

Figure 8: Flow chart of the procedure to calculate a target load, avoiding the pitfalls mentioned in the text (e.g. computing a target load that allows violation of the criterion *after* the target year).

The first check at every site is, whether the critical load (CL) is exceeded in the reference year (2010 in our case). If the answer is 'yes' (as for the soils with CEC=40 and 60 in Fig.6), the next step is to run the dynamic model with the deposition equal to the critical load. If in the target year the chemical criterion is no longer violated (e.g. Al/Bc$\leq$1), the target load equals the critical load (TL=CL).

If, after running the model with the critical load as deposition, the criterion is still violated in the target year, the model has to be run with "zero" deposition until the specified target year. "Zero" deposition means a deposition small enough as not to contribute to acidification (or eutrophication). In the case of nitrogen this would mean that N_{dep} is set equal to $CL_{min}(N)$, thus avoiding problems, e.g. negatively influencing forest growth in case of zero N deposition.

If, after running the model with "zero" deposition, the criterion is still violated in the target year, then the target cannot be met in that year. In such a case recovery can only be achieved in

a later year. Otherwise, a target load exists and has to be calculated; its value lies somewhere between zero and the critical load.

If the critical load is not (or no longer) exceeded in 2010 (as for the soil with CEC=80 in Fig.6), this does *not* mean that the risk of damage to the ecosystem is already averted – it only means that *eventually*, maybe after a very long time, the chemical criterion is no longer violated. Only if, in addition, the chemical criterion is not violated in 2010, no further emission reductions are required for that ecosystem. Also, if the model is run with the 2010 deposition until the target year and the criterion is no longer violated in that year, no further emission reductions are required. If the criterion is still violated in the target year, the procedure continues with running the model with "zero" deposition etc (see Figure 8).

In the implementation of the above procedure one could skip the step in which the model is run with the critical load as deposition (in case of exceedance in 2010) and immediately start with target load calculations (if a target load exists). And only afterwards check if this target load is greater than CL (and set it to CL) (see soil with CEC=60 in Fig.7). However, in view of the fact that TL calculations require iterative model runs, and also to avoid surprises due to round-off errors, it makes good sense to include that intermediate step.

An issue requiring attention in all target load calculations is the assumptions about finite nitrogen buffers. If it is, e.g., assumed that a soil can immobilise N for (say) the next 50 years to a larger degree than assumed in the critical load calculations, then target loads will always be higher than the critical load. This might cause confusion and demands careful explanations.

When summarising target load calculations for ecosystems in a grid square (or region) it is important not only to report those sites for which target load (functions) have been derived, but all three cases (and their areas), i.e. the sites for which (i) no further deposition reductions are necessary, (ii) a target load has been calculated, and (iii) no target load exists (for the given target year). Note that in case (i), the 2010 deposition has necessarily to be below (or equal to) the critical load.

6.2   Presentation of model results

For single site applications of dynamic models the obvious way to present model output are graphs of the *temporal development of* the most relevant *soil chemical variables*, such as base saturation or the concentrations of ions in the soil solution (e.g. Al/Bc-ratio), in response to given deposition scenarios. In regional (European) applications, however, this kind of information has to be summarised. This can be done in several ways, e.g., by displaying the temporal development of selected percentiles of the cumulative distribution of the variable(s) of interest (see Figure 9 and, e.g., Kurz et al. 1998). Another way is to show a sequence of maps displaying the variable of interest in (say) five-year intervals ('map movies'). Other options are discussed and illustrated in Evans et al. (2001) and Jenkins et al. (2002).
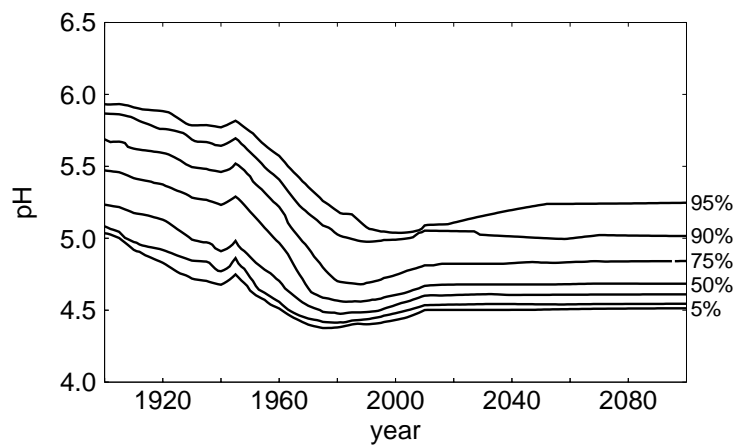
Figure 9: Example of percentile traces of a regional dynamic model output (Kurz and Posch 2002). From it 7 percentiles (5, 10, 25, 50, 75, 90 and 95%) can be read for every time step.

Maps can represent single sites only if their number does not become too large. If the number of sites reaches the thousands, statistical descriptors (means, percentiles) have to be used to represent the model output. For example, for a given target year the percentage of ecosystems in a grid square for which the target is reached under a given deposition scenario can be displayed in a map format, very much in the same way as protection percentages (derived from protection isolines) have been displayed for critical load exceedances. The procedures for calculating percentiles and 'target load' isolines can be found in Posch et al. (1995) and the Mapping Manual.

Annex A: Biological response models

Just as there are delays between changes in acid deposition and changes in surface (or soil) water chemistry, there are delays between changes in chemistry and the biological response. Because the goal in recovery is to restore good or healthy population of key indicator organisms, the time lag in response is the sum of the delays in chemical and biological response. Thus dynamic models for biological response are needed.

Terrestrial ecosystems

A major drawback of most dynamic soil acidification models is the neglect of biotic interactions. For example, vegetation changes are mainly triggered by a change in N cycling (N mineralisation; Berendse et al. 1987). Furthermore the enhancement of diseases by elevated N inputs, such as heather beetle outbreaks, may stimulate vegetation changes (Heil and Bobbink 1993). Consequently, dynamic soil-vegetation models, which include such processes, have a better scientific basis for the assessment of critical and target N loads. Examples of such models are CALLUNA (Heil and Bobbink 1993) and ERICA (Berendse 1988). The model CALLUNA integrates N processes by atmospheric deposition, accumulation and sod removal, with heather beetle outbreaks and competition between species, to establish the critical N load in lowland dry-heathlands (Heil and Bobbink 1993). The wet-heathland model ERICA incorporates the competitive relationships between the species *Erica* and *Molinia*, the litter production from both species, and nitrogen fluxes by accumulation, mineralisation, leaching, atmospheric deposition and sheep grazing. At present there are also several forest-soil models that do calculate forest growth impacts in response to atmospheric deposition and other environmental aspects, such as meteorological changes (precipitation, temperature) and changes in CO_2 concentration. Examples are the models NAP (Van Oene 1992), ForSVA (Oja et al. 1995) and Hybrid (Friend et al. 1997).

Biological dose/response models related to impacts on species diversity in terrestrial ecosystems have up to now not focussed on the time-dynamic aspects. Instead, statistical models have been developed to assess the relationship between the species diversity of the ecosystem and abiotic aspects related to acidification and eutrophication. An example is the vegetation model MOVE (Latour and Reiling 1993), that predicts the occurrence probability of plant species in response to scenarios for acidification, eutrophication and desiccation. Input to the model comes from the output of the soil model SMART2 (Kros et al. 1995), being an extension of SMART (De Vries et al. 1989, Posch et al. 1993). The SMART2 model predicts changes in abiotic soil factors indicating acidification (pH), eutrophication (N availability) and desiccation (moisture content) in response to scenarios for acid deposition and groundwater abstraction, including the impact of nutrient cycling (litterfall, mineralisation and uptake). MOVE predicts the occurrence probability of ca 700 species as a function of three abiotic soil factors, including nitrogen availability, using regression relationships. Since combined samples of vegetation and environmental variables are rare, the indication values of plant species by Ellenberg (1985) are used to assess the abiotic soil conditions. Deduction of values for the abiotic soil factors from the vegetation guarantees ecological relevance. Combined samples of vegetation with environmental variables are used exclusively to calibrate Ellenberg indication values with quantitative values of the

abiotic soil factors. A calibration of these indication values to quantitative values of the abiotic soil factors is necessary to link the soil module to the vegetation module.

A comparable statistical model is the NTM model (Schouwenberg et al. 2000), that was developed to predict the potential conservation value of natural areas. Normally conservation values are calculated on the basis of plant species or vegetation types. As with MOVE, NTM has the possibility to link the vegetation and the site conditions by using plant ecological indicator values. NTM uses a matrix of the habitats of plant species defined on the basis of moisture, acidity and nutrient availability. The model was calibrated using a set of 160,252 vegetation relevees. A value index per plant species was defined on the basis of rarity, decline and international importance. This index was used to determine a conservation value for each relevee. The value per relevee was then assigned to each species in the relevee and regressed on the Ellenberg indicator values for moisture, acidity and nutrient availability (Ellenberg 1985) using a statistical method (P-splines). The model has these three Ellenberg indication values as input for the prediction of the potential conservation value. A potential conservation value is calculated for a combination of the abiotic conditions and vegetation structure (ecotope). Therefore four vegetation types are accounted for, each represented by a submodel of NTM: heathland, grassland, deciduous forest and pine-forest. Use of those models in dynamic modelling assessments is valuable to gain more insight in the effect of deposition scenarios on terrestrial ecosystems.
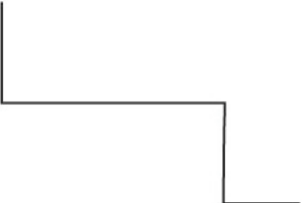
Aquatic ecosystems

As with terrestrial ecosystems, biological dose/response models for surface waters have not generally focussed on the time-dynamic aspects. For example, the relationship between lake ANC and brown trout population status in Norwegian lakes used to derive the critical limit in the Mapping Manual is based on synoptic (once in time) surveys of ANC and fish status in a large number of lakes. Similarly the invertebrate indices (Raddum 1999) and diatom response models (Allot et al. 1995, Battarbee et al. 1996) do not incorporate time-dynamic aspects. Additional information on dose/response comes from traditional laboratory studies of toxicity (chronic and acute) and reproductive success.

Information on response times for various organisms comes from studies of recovery following episodes of pollution, for example, salmon population following chemical spill in a river. For salmon full recovery of the population apparently requires about 10 years after the water chemistry has been restored.

There are currently no available time-dynamic process-oriented biological response models for effects of acidification on aquatic and terrestrial organisms, communities or ecosystems. Such models are necessary for a full assessment of the length of time required for recovery of damage from acidification.

There are several types of evidence that can be used to empirically estimate the time delays in biological recovery. The whole-lake acidification and recovery experiments conducted at the Experimental Lakes Area (ELA), north-western Ontario, Canada, provide such information at realistic spatial and temporal scales. These experiments demonstrate considerable lag times between achievement of acceptable water quality following decrease in acid inputs, and achievement of acceptable biological status. The delay times for various organisms are at least several years. In the case of several fish species irreversible changes may have occurred (Hann and Turner 2000, Mills et al. 2000).

A second source of information on biological recovery comes from liming studies. Over the years such studies have produced extensive empirical evidence on rate of response of individual species as well as communities following liming. There has been little focus, however, on the processes involved.

Finally there is recent documentation of recovery in several regions at which acid deposition has decreased in the 1980s and 1990s. Lakes close to the large point-source of sulphur emissions at Sudbury, Ontario, Canada, show clear signs of chemical and biological recovery in response to substantial decreases in emissions beginning in the late 1970s (Keller and Gunn 1995). Lakes in the nearby Killarney Provincial Park also show clear signs of biological recovery during the past 20 years (Snucins et al. 2001). Here there are several biological factors that influence the rate of biological recovery such as:
(1) fish species composition and density
(2) dispersal factors such as distance to intact population and ability to disperse
(3) existence of resting eggs (for such organisms such as zooplankton)
(4) existence of precluding species – i.e. the niche is filled.
Recently, a workshop held under the auspices of the UNECE reviewed the current knowledge on models for biological recovery in surface waters (see Wright and Lie 2002).

Future work on biological response models must also include consideration of the frequency and severity of harmful episodes, such as pH shocks during spring snowmelt, or acidity and aluminium pulses due to storms with high seasalt inputs. These links between episodic water chemistry and biological response at all levels (organisms, community, and ecosystem) are poorly quantified and thus not yet ready to be incorporated into process-oriented models.

Annex B: Base saturation as a critical limit

Finite buffers, such as cation exchange capacity and its base saturation, are not considered in the derivation of critical loads, since they do not influence steady-state situations. However, this does *not* mean that the state of those buffers is not influenced by the steady state! The relationship between the base saturation, E_{Bc}, and the Al/Bc-ratio can be easily derived for the Bc-Al-H exchange system. When using Gaines-Thomas equations, inserting E_{Al} and E_H from eqs.3.12 into eq.3.15 and using eq.3.8 (see section 3.2) to express $[H]$ in terms of $[Al]$ yields:

$$\text{(B1)} \qquad E_{Bc} + E_{Bc}^{3/2} \frac{r_{eq} K_{AlBc}^{1/2}}{[Bc]^{1/2}} + E_{Bc}^{1/2} \frac{r_{eq}^{1/\alpha} K_{HBc}^{1/2}}{K Al_{ox}^{1/\alpha} [Bc]^{1/2 - 1/\alpha}} = 1$$

where $r_{eq} = [Al]/[Bc]$ is the equivalent Al/Bc-ratio. This cubic equation in $E_{Bc}^{1/2}$ can easily be solved numerically to obtain the base saturation as function of the (critical) Al/Bc-ratio (Figure Ba). As can be seen, for average values of the equilibrium constants and a wide range of base cation concentrations ($[Bc] = (Bc_{dep} + Bc_w - Bc_u)/Q$ in steady state), the widely-used value of $(Al/Bc)_{crit} = 1$ corresponds to very low (steady-state) base saturation values. The same picture emerges when using the Gapon exchange model. In this case the equations can be solved explicitly for the base saturation:

$$\text{(B2)} \qquad E_{Bc} = \frac{1}{1 + \dfrac{r_{eq}^{1/3} k_{AlBc}}{[Bc]^{1/6}} + \dfrac{r_{eq}^{1/\alpha} k_{HBc}}{K Al_{ox}^{1/\alpha} [Bc]^{1/2 - 1/\alpha}}}$$

and in Figure Bb it is shown as function of the (critical) molar Al/Bc-ratio.

Figure B indicates that the path to steady state can lead to a substantial loss of the pool of exchangeable base cations. This could be at odds with ensuring the overall viability of forests and forest soils, and a critical (acceptable, minimum) base saturation could be chosen as a criterion for calculating critical acidity loads in order to avoid (large) losses of base cations (see Hall et al. 2001, UNECE 2001b). It is also interesting to note that base saturation is 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).
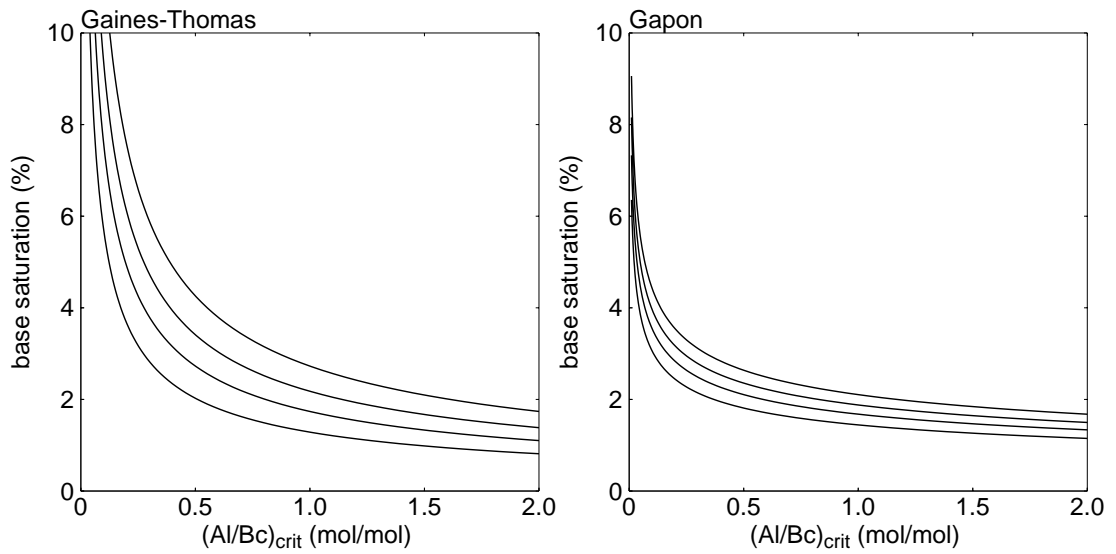
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Figure B: Base saturation as a function of the (critical) molar Al/Bc-ratio for 4 different base cation concentrations ($[Bc]$= 20 (lowest curve), 50, 100 and 200 meq/L (highest curve); α=3 and KAl_{ox}=10^8 (mol/L)$^{-2}$). (a) For the Gaines-Thomas exchange equations (K_{AlBc}=1 mol/L, K_{HBc}=10^5 (mol/L)$^{-1}$), and (b) for Gapon exchange equations (k_{AlBc}=10 (mol/L)$^{1/6}$, k_{HBc}=10 (mol/L)$^{-1/2}$).

Annex C: Unit conversions

For convenience we use the term 'equivalents' (eq) instead of the SI-unit 'moles of charge' (mol_c). If X is an ion with molecular weight M and charge z, then one has:

(C1) $$1\,g\,X = \frac{1}{M}\,mol\,X = \frac{z}{M}\,eq\,X$$

Obviously, moles and equivalents are the same for $z=1$.

When dealing with equations of chemical equilibria, the unpleasant task of converting the equilibrium constants to the required units often arises. In the following we give a formula which should cover most of the cases encountered: Let A and B be two chemical compounds in the following equilibrium equation:

(C2) $$[A^{m\pm}]^x = K[B^{n\pm}]^y$$

where the square brackets [...] denote concentrations in mol/L (L stands for litre), implying for the equilibrium constant K the units $(mol/L)^{x-y}$. If the concentrations are to be expressed in eq/V, where V is an arbitrary volume unit with $1L=10^cV$, then the equilibrium constant in the new units is given by

(C3) $$K' = K \cdot 10^{c(y-x)}\frac{m^x}{n^y}\,(eq/V)^{x-y}$$

Note: To convert to mol/V, set $m=n=1$ in the above equation; and to covert to g/V set $m=1/M_A$ and $n=1/M_B$, where M_A and M_B are the molecular weights of A and B, resp.

Example 1: The gibbsite equilibrium is given by $[Al^{3+}]=K[H^+]^3$, i.e. $m=3$, $x=1$, $n=1$, $y=3$ and (e.g.) $K=10^8 (mol/L)^{-2}$. To convert to eq/m^3, one has $c=-3$ and thus $K' = 10^8 \cdot 10^{-3\cdot(3-1)} \cdot 3 = 300\,(eq/m^3)^{-2}$.

The above reasoning can also be used for converting exchange constants. For example, the Gapon equation for Al-Bc exchange can be written as

(C4) $$\frac{E_{Al}}{E_{Bc}}[Bc^{2+}]^{1/2} = k_{AlBc}[Al^{3+}]^{1/3}$$

and since exchangeable fractions are dimensionless, eq.C3 can be used.

Example 2: Let $\log_{10}k_{AlBc}=0$; then $k_{AlBc}=10^0=1(mol/L)^{1/6}$ ($x=1/2$, $y=1/3$). Since $m=2$ and $n=3$, one gets when converting to eq/m^3, i.e. $c=-3$, $k_{AlBc}=1\cdot 10^{-3\cdot(1/3-1/2)} \cdot (2^{1/2}/3^{1/3}) = 3.100806$ $(eq/m^3)^{1/6}$.
And for k_{HBc} the multiplier to obtain $(eq/m^3)^{-1/2}$ is $0.002^{1/2}=0.0447213$.
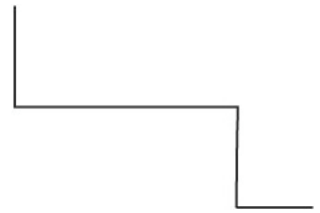
Annex D: Averaging soil profile properties

For single layer soil models, such as VSD, SMART or MAGIC, the profile averages of certain soil parameters are required. In the following we give the formulae for the average bulk density ρ (g/cm^3), cation exchange capacity CEC (meq/kg) and base saturation E_{BC}.

For a given soil profile we assume that there are measurements of bulk density ρ_l cation exchange capacity CEC_l and base saturation $E_{BC,l}$ for n (homogeneous) soil horizons with thickness z_l (l=1,..., n). Obviously, the total thickness (soil depth) z is given by

(D1)
$$z = \sum_{l=1}^{n} z_l$$

and the mean bulk density ρ of the profile is derived from mass conservation (per unit area):

(D2)
$$\rho = \frac{1}{z} \sum_{l=1}^{n} z_l \rho_l$$

The average cation exchange capacity CEC has to be calculated in such a way that the total number of exchange sites (per unit area) is given by $z \cdot \rho \cdot CEC$. This implies the following formula for the profile average cation exchange capacity:

(D3)
$$CEC = \frac{1}{z\rho} \sum_{l=1}^{n} z_l \rho_l CEC_l$$

And for the average base saturation of the profile we get then:

(D4)
$$E_{BC} = \frac{1}{z\rho CEC} \sum_{l=1}^{n} z_l \rho_l CEC_l E_{BC,l}$$

NB: For aquatic ecosystems, these parameters have to be averaged over the catchment area as well.

Annex E: Measuring techniques for soil data

An overview of the various measuring methods that can be used when gathering new soil data is given in Table E-1. The data are arranged according to their importance.

Table E-1: Measuring techniques for soil data

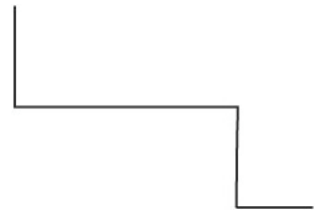| Variable	Measuring techniques
CEC	Extraction with NH_4-acetate buffered at pH 6.5 or 0.01 N AgTu unbuffered
E_{BC}[1]	Extraction with an unbuffered solution e.g., i.e. $BaCl_2$
E_{Al}	ibid
ρ	Sampling a fixed volume and weighting
C_{lt}	Kurmies method (wet digestion)
N_{lt}	Kjeldahl method (wet digestion)
K_{XY}	Centrifugation of a soil sample in which H, Al, Ca, Mg, K, Na and NH_4 are measured at the adsorption complex and in the soil solution
Ca_{cb}	Wesemael method (weight loss) or Scheibler method (CO_2 evolution)
Al_{ox}	Etraction with NH_4-oxalate buffered at pH 5.5
S_{max}	Adding SO_4 at a concentration of 200 mg/l and extraction of the amount at the complex with 0.016 N NaH_2PO_4

[1] BC (Ca, Mg, K and Na) can also be measured in a buffered solution

The cation exchange capacity should be measured in a buffered solution in order to standardise to one pH value. There are two possibilities in this respect: use of bariumchloride - tri-ethanolamine ($BaCl_2$-TEA) buffered at pH 8.2 or ammonium - acetate (NH_4OAC) buffered at pH 6.5. Since cation exchange plays a major role in non-calcareous soils with a maximum pH near 6.5, the NH_4OAC method is used. The principle of this method is the measurement of the NH_4 concentration after percolation (column experiment) or shaking (batch experiment) of a soil sample with a solution of a known NH_4 concentration. The removal of NH_4 is equal to the CEC.

The base cation fraction at the adsorption complex can be measured in the ammonium - acetate percolate. However, in order to measure the Al fraction at the adsorption complex, it is necessary to use an unbuffered solution. In this respect there are various possibilities, including an unbuffered $BaCl_2$ method. The concentrations of Al, Ca, Mg (and possibly Na and K) in the percolate are measured by atomic emission (ICP) or atomic adsorption spectrophotometry (AAS). The fraction of H at the adsorption complex is derived by subtracting the sum of Al, Ca, Mg, K and Na from the CEC.

The carbonate content of the soil can be measured by adding a strong acid (generally HCl) and measuring the weight loss or the CO_2 evolution of the soil sample. The first method (Wesemeal) is fast but less accurate, whereas the second method (Scheibler) is time demanding but more accurate.

The amount of Al in hydroxides which buffer the acid lead can be extracted by various methods e.g. pyrophosphate, ammonium-oxalate and dithionite. The second method is recommended since laboratory experiments indicate that this gives a good indication of the reactive amount of Al.

Carbon and nitrogen in litter can be determined after wet digestion using a mixture of H_2O_2. Total C and total N can than be determined by the Kurmies and Kjeldahl method respectively.

Exchange constants for H and Al versus Ca+Mg (BC) can be derived by measuring the concentrations of H, Ca, Mg and Al in the soil solution, which can be extracted by centrifugation. This should be done in samples where the amount at the adsorption complex is also measured. In this way, exchange constants have been derived for different layers (horizons) of acid sandy soils in the Netherlands (Kleijn et al. 1989).

Measurement of S_{max} requires a laboratory experiment, which is rather time-consuming. The principle of this method is described in Johnson and Todd (1983).

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