UPDATE TO:
THE STATUS OF UK CRITICAL LOADS
CRITICAL LOADS METHODS, DATA & MAPS

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EXECUTIVE SUMMARY

This document provides the latest update to the critical loads for acidity and nitrogen for sensitive UK habitats, which have been made in the light of new research findings and revisions to some of the underlying data sets used for calculating critical loads.

This report focuses on the updates made in preparation for submitting UK critical loads of acidity and nitrogen to the UNECE's Coordination Centre for Effects (CCE) on 31st March 2004. The CCE use these data in compiling European-scale critical load maps for work under the UNECE Convention on Long-Range Transboundary Air Pollution. This report is an update to the February 2003 UK Status Report published on the UK National Focal Centre (NFC) web site: http://critloads.ceh.ac.uk.

The main changes this year are summarised below:

- The critical chemical criterion used in the calculation of acidity critical loads for woodlands occurring on organo-mineral soils has been updated to the molar ratio of calcium to aluminium equal to one in soil solution, on the basis that the soil water aluminium must be accounted for when considering acidification processes in these soils. (Section 3.3)
- The number of freshwater sites in acidified regions for which acidity critical loads are calculated has been increased using new survey information. (Section 5.2)
- The value of the critical chemical threshold of acid neutralising capacity (ANC) used in the calculation of acidity critical loads for freshwaters has been changed from zero to 20μeql^{-1} for all sites, except for naturally acidic sites where a value of ANC 0μeql^{-1} has been retained. (Section 5.5)

For further information on the data and methods used in the calculation of acidity and nutrient nitrogen critical loads not covered in this report, please refer to the February 2003 report (http://critloads.ceh.ac.uk).

The NFC is currently calculating acidity and nutrient nitrogen critical load exceedances, ie, the amount of excess deposition above the critical load. The exceedance results will be published in an Addendum to this report in April 2004.

1. INTRODUCTION TO CRITICAL LOADS

1.1 Introduction

The air pollutants sulphur dioxide, nitrogen oxides and ammonia can contribute to acidification, and nitrogen oxides and ammonia can contribute to terrestrial eutrophication. Both problems can adversely affect semi-natural ecosystems. The National Expert Group on Transboundary Air Pollution recently reviewed the impacts of air pollutants on UK ecosystems and prospects for the future (NEGTAP, 2001). Measuring and quantifying the potential ecological damage by air pollutants is not a simple matter. The common measure, used across Europe since the 1980s, is the critical load. This is defined as 'a quantitative estimate of the exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge' (Nilsson & Grennfelt, 1988).

The amount of deposited pollutant that exceeds the critical load of acidity or nutrient nitrogen, is called the 'exceedance'. Exceedance of critical loads represents the potential for damage, but is not a quantitative estimate of damage to the environment. The critical load is an equilibrium concept and gives no information on the timescales for damage (when the critical load is exceeded) or recovery (when deposition is reduced below the critical load). Timescales for damage and recovery vary greatly, depending on the environmental receptor and the pollutant combination; to estimate these dynamic models are required. Such models are being developed under Defra contracts and under the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP), but are not discussed in this Report.

The application of critical loads has proved very useful for policy development. It provides an 'effects-based' approach where the environmental benefits of emission reductions can be gauged. Closing the gap between estimated pollutant deposition (above the critical load) and the critical load, for ecosystems across Europe, is one of the main drivers of emission control agreements under the UNECE CLRTAP, the EC European Acidification Strategy, and Clean Air For Europe.

National critical loads data are submitted to the Coordination Centre for Effects (CCE) in the Netherlands in response to calls for data for work under the UNECE CLRTAP. The critical loads described in this report form the March 2004 UK data submission.

1.2 Calculation and Mapping of Critical Loads

The preparation of Critical Loads maps has two main components: (i) mapping the distribution of the main habitats and (ii) calculation of critical loads to assign to those habitats. Critical loads are applied to a number of Biodiversity Action Plan (BAP) Broad Habitats sensitive to acidification and/or eutrophication (Table 1.1). The derivation of the national maps of these habitats are described in detail in the February 2003 UK Status Report (Hall *et al.*, 2003). The habitat maps remain unchanged with the exception of minor modifications to the managed woodland habitat maps (Chapter

2). In order to harmonise the naming and classification of habitats across Europe, habitat codes from the European Nature Information System (EUNIS, Davies & Moss 2002) are also assigned to each habitat (Table 1.1) prior to the data submission to the CCE.

Table 1.1. Broad Habitats mapped for acidity and nutrient nitrogen critical loads

Broad Habitat[1]	**EUNIS class(es)**[1]	**Critical loads for:**	
		Acidity	**Nutrient nitrogen**
Acid grassland	Dry acid & neutral closed grassland (E1.7) Moist or wet oligotrophic grassland (E3.5)	✓ ✓	✓ ✓
Calcareous grassland	Semi-dry calcareous grassland (E1.26)	✓	✓
Dwarf shrub heath	Northern wet heaths (F4.11) Dry heaths (F4.2)	✓ ✓	✓ ✓
Bogs	Raised & blanket bogs (D1)	✓	✓
Montane	Moss & lichen dominated summits (E4.2)	✓	✓
Coniferous woodland (managed)	Coniferous woodland (G3)	✓	✓
Broadleaved woodland (managed)	Broadleaved woodland (G1)	✓	✓
Unmanaged woodland	Broadleaved & coniferous woodland (G1 & G3)	✓	✓
Supralittoral sediment	Shifting coastal dunes (B1.3) Coastal stable dune grassland (B1.4)	× ×	✓ ✓
Standing open water[2]	Surface standing waters (C1)	✓	×
Rivers & streams[2]	Surface running waters (C2)	✓	×

[1]Please refer to the February 2003 UK Status Report (Hall *et al.*, 2003) for more information on habitat mapping and the relationships between the BAP Broad Habitats and EUNIS habitat classes.
[2] Acidified freshwaters in UK are assumed not to be susceptible to eutrophication, due to phosphorus limitation.

A number of methods exist to determine the critical loads of acidity or nutrient nitrogen, which fall into two broad categories (i) mass balance and (ii) empirical approaches. In the mass balance approach, the long term chemical inputs and outputs (affecting acidity or nitrogen) are calculated, and the critical load is exceeded when the critical chemical criterion is breached. The chemical criterion is chosen to reflect a change in the ecosystem which would lead to damage. In the empirical approach, the critical load is estimated rather than calculated, based on expert interpretation of experimental and field evidence for the ecosystem response to deposition.

Appropriate methods, critical chemical criteria and ranges for empirical critical loads are agreed at the UNECE level under the International Cooperative Programme on Modelling and Mapping. These methods are summarised in the UNECE's Mapping Manual (http://www.umweltbundesamt.de/mapping). The methods currently used in the UK to calculate acidity and nutrient nitrogen critical loads are consistent with the Mapping Manual and are summarised in Table 1.2.

Table 1.2 Summary of the methods used to calculate critical loads for sensitive habitats in the UK

Habitat type	**Method to assign critical load for acidity**	**Method to assign critical load for nutrient nitrogen**
Non-woodland terrestrial habitats	Empirical, based on dominant soil type	Empirical
Unmanaged woodland	Steady State Mass Balance	Empirical
Managed woodland	Steady State Mass Balance	Steady State Mass Balance
Surface water lakes and streams	First Order Acidity Balance [FAB]	Not used[1]

This report describes the updates made to the methods for calculating acidity critical loads in preparation for the data submission to the CCE in March 2004. The methods have been updated for:

- Managed and unmanaged woodland habitats (Section 3.3)
- Freshwater lakes and streams (Chapter 5)

In addition, minor revisions have been made to the acidity critical loads map for peat soils (Section 3.2), which have had a small effect on the critical load maps for the terrestrial habitats.

The critical loads of nutrient nitrogen remain unchanged from the February 2003 data submission (Hall *et al.*, 2003) and are not described in this report.

1.3 Calculation and mapping of critical load exceedances

Critical loads are compared with acidifying or eutrophying deposition to determine the excess deposition above the critical load, ie, the exceedance.

Exceedance = Deposition – Critical Load

For eutrophication, the exceedance is calculated using total nitrogen deposition (derived from nitrogen oxides and ammonia). For acidification, the contribution of both sulphur and nitrogen compounds must be taken into account, and this is done using the Critical Loads Function (CLF, Chapter 4). The CLF was developed in Europe (Posch *et al.*, 1999; Posch & Hettelingh, 1997; Posch *et al.*, 1995; Hettelingh *et al.*, 1995). It defines separate acidity critical loads in terms of sulphur and nitrogen, referred to as the “minimum” and “maximum” critical loads of sulphur and nitrogen. It is these “minimum” and “maximum” critical loads that are used in the calculation of critical loads exceedance for acidity.

In addition, the “accumulated exceedance” (AE) can be calculated, where exceedance is summed over the whole habitat area:

AE = exceedance * exceeded habitat area

Therefore, the AE is a measure of exceedance that takes into account ***both the magnitude of exceedance and the habitat area exceeded.***

A summary of exceedance statistics for each habitat will be provided in an Addendum to this report in April 2004.

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2. HABITAT MAPPING

In 2003 critical loads of acidity and nutrient nitrogen were applied to sensitive UK Biodiversity Action Plan (BAP) Broad Habitats. The methods used to map these habitats are described in detail in Hall *et al.* (2003). No changes to the methods have been made this year. However, updates to other data sets have led to minor changes in the habitat distribution maps for managed woodlands and for calcareous grassland. These changes are described below.

2.1 Changes to managed woodland habitat distribution maps

Upon the advice of Forest Research (FR) we have made minor changes to the habitat distributions for managed coniferous and managed broadleaved woodland. Previously FR provided data on the area in each 1km grid square of three woodland types:

(i) managed coniferous woodland
(ii) managed broadleaved woodland
(iii) unmanaged coniferous and broadleaved woodland.

This year, whilst re-visiting the acidity critical load methods to be applied to woodland on different soil types (Section 3.3) it became apparent that there were areas of managed broadleaved woodland mapped in grid squares dominated by peat soils. FR considered this unlikely, and suggested it was more likely that they were young coniferous trees. This discrepancy has arisen because in the 2002-03 mapping exercise, the decision was made to map young trees (undefined in the source data from the National Inventory of Woodland and Trees: FC, 2003) as managed broadleaved woodland. FR therefore recommended that these woodland areas be removed from the managed broadleaved woodland map and added to the managed coniferous woodland map.

The original data sets from the FR were duly modified and the habitats re-mapped using the combination of FR and CEH Land Cover Map 2000 (Fuller *et al.*, 2002) data using the methods described in Hall *et al.* (2003). The changes in the overall woodland habitat areas are given in Table 2.1.

Table 2.1. The area of UK woodland habitats as mapped using a combination of FR and CEH Land Cover Map 2000 data.

Woodland habitat	February 2003 Area (km^2)	February 2004 Area (km^2)	% change in area
Managed conifer	7971	8377	+ 5.1%
Managed broadleaved	7554	7452	- 1.4%
Unmanaged	4011	4011	No changes made

These changes in the woodland areas mapped are reflected in the critical load maps derived for these habitats and in the data submitted to the CCE.

2.2 Changes to calcareous grassland habitat distribution map for acidity

The area of calcareous grassland mapped for acidity critical loads has decreased by 0.2%. This is because some of the 1km calcareous grassland square mapped for nutrient nitrogen coincide with 1km squares that have low empirical soil critical loads (ie, below 2.0 keq ha^{-1} $year^{-1}$). The soil acidity critical loads are based on the dominant soil type in each 1km grid square; soils derived from base-poor rocks are more acid and result in low critical loads. Calcareous grassland may occur in 1km grid squares that have a low acidity critical load, but is unlikely to be found on the acid soil determining the low critical load. Changes to the acidity critical loads map for peat soils have resulted in more squares where the critical load value would be inappropriate for calcareous grassland, and hence the area of this habitat mapped for acidity has been reduced.

The area of calcareous grassland mapped for nutrient nitrogen remains unchanged (Hall *et al.*, 2003).

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3. CRITICAL LOADS OF ACIDITY FOR TERRESTRIAL HABITATS

3.1 Introduction

In December 2003 a group of experts from the NFC and the Defra Terrestrial Umbrella met to review the methods of acidity critical loads for (a) peat soils (b) woodland on mineral, organic and peat soils. The sections below summarise the methods used and any changes made as a result of this meeting.

3.2 Critical loads of acidity for soils

Critical loads are assigned to each 1km square according to the dominant soil type occurring in each square. The critical loads are calculated using two methods: one for mineral and organo-mineral soils and another for peat soils. The combination of the critical loads for all soil types into a single map produces a map called the empirical critical loads of acidity for soils. This map forms the basis of the acidity critical loads for areas of non-woodland terrestrial habitats.

The methodology for calculating and mapping acidity critical loads for mineral and organo-mineral soils remains unchanged from previous years (Hall *et al.*, 2003; Hornung *et al.*, 1995). Critical load values are assigned according to the mineralogy and weathering rate of the dominant soil (series or map unit) in each 1km grid square.

The method applied to peat soils was reviewed and is presented below. A modification has subsequently been made to the allocation of critical load values to fenland peat soils.

3.2.1 Critical loads of acidity for peat soils

For the February 2003 data submission the method for calculating acidity critical loads for peat soils was changed from that used previously (Hall *et al.*, 2003). The updated method set the critical load to the amount of acid deposition that would give rise to an effective rain pH of 4.4. The following equation was used to calculate the acidity critical load for all UK 1km grid squares dominated by peat soils:

$$CLA = Q * [H^+]$$

Where:
Q = runoff in metres
$[H^+]$ = critical hydrogen ion concentration equivalent to pH 4.4

This method is supported by UK data published by Calver (2003), Skiba & Cresser (1989) and Calver *et al*. (2004, in press).

The meeting between UK soil critical load experts discussed how this method related to those applied to other soil types and whether this effective rain pH could be translated into a critical soil solution pH, a commonly used criterion in the Simple

Mass Balance (SMB) equation. It was agreed that the corresponding soil solution pH to an effective rain pH of 4.4, would also be pH 4.4. Therefore the method used for peat soils in February 2003 still stands and can be expressed as an SMB with a criterion of critical soil solution pH 4.4. The equation used remains the same as that above, as the leaching of aluminium and base cation weathering, as included in the SMB equation (Appendix 1), can both be set to zero for peat soils.

This method is applicable to upland and lowland acid peat soils, but not to the lowland/arable fen peats. The peat soils in these lowland/arable fen areas are not as sensitive to acidification as those in other regions and therefore require a higher critical load to be set. The critical loads for the lowland/arable fen areas were re-set to 4.0 keq ha^{-1} $year^{-1}$; this high value is at the top of the empirical range of critical load values for soils (Hornung et al, 1995). In February 2003 the lowland/arable fen areas were defined by selecting any 1km square dominated by peat soil that also contained any arable land, according to the Land Cover Map 2000 (LCM2000). When this method was reviewed in December 2003, it was agreed that the critical load of 4.0 keq ha^{-1} $year^{-1}$ had been set for some areas that would not in fact be considered to be lowland/arable fen. To refine this, a map was created identifying this habitat as those squares that are not only dominated by peat soil, but where arable is the dominant land cover according to LCM2000. This reduced the number of 1km squares requiring the critical load to be re-set to 4.0 keq ha^{-1} $year^{-1}$ from 2829 to 514; subsequently the mean acidity critical load for the peat-dominated squares across the UK was reduced from 1.1 keq ha^{-1} $year^{-1}$ to 0.8 keq ha^{-1} $year^{-1}$. The February 2003 and February 2003 acidity critical loads maps for the peat-dominated 1km squares in the UK are shown in Figure 3.1.

Changes in the methods are summarised in Tables 3.1 and 3.2.

3.3 Critical loads of acidity for woodland habitats

For the February 2003 data submission different methods were applied to the calculation of acidity critical loads for woodlands on mineral, organic and peat soils (Hall *et al.*, 2003). These methods are summarised in Table 3.1.

When reviewing the methods in December 2003 the following recommendations were made to Defra and have subsequently been incorporated in the 2004 critical loads datasets:

(i) Critical loads continue to be applied to managed and unmanaged woodlands in the UK. Critical loads are required to protect these habitats and to protect the land under managed conifer forest for future non-forest use and possible reversion to semi-natural land uses.

(ii) The soil types classified as “organic” are really “organo-mineral” soils, ie, mineral soils with a peaty top. Therefore soil water aluminium must be accounted for when considering acidification processes in these soils and must therefore be included in the criterion used in the SMB.

(iii) To address the issue in (ii), the criterion used in the SMB for these “organo-mineral” soils was re-considered. The critical soil solution pH 4.0 used for the February 2003 data submission is recommended in the UNECE Mapping Manual (UBA, 1996) as a method for organic soils. The origin of the critical

soil solution value of pH 4.0 (de Vries, 1991) shows it was derived via the gibbsite equilibrium and a specified critical inorganic Al concentration of 0.2 mol_c m^{-3}, from soil solution data for eight Douglas fir stands in the Netherlands. As this criteria is effectively based on an Al concentration, it was agreed that it is more justifiable to maintain consistency of approaches for both mineral and organo-mineral soils and so the molar soil solution ratio of Ca:Al=1 criteria has been applied to both soil types.

(iv) The gibbsite coefficient (kgibb) in the SMB equation is set to 950 m^6 eq^{-2} for mineral soils. For the organo-mineral soils expert judgement recommended using a gibbsite coefficient of 100 m^6 eq^{-2} on the basis that the tree roots are largely limited to the upper soil horizons because sub-soil conditions such as frequent waterlogging in heavy textured soils can often inhibit root development below the surface organic layer.

(v) The application of phosphate and potassium fertilisers (primarily rock phosphate and muriate of potash) as a contribution to the base cation budget to managed woodlands has been taken into account in the calculation of acidity critical loads for the managed woodlands on organo-mineral and peat soils. Forest Research provided fertiliser application rates based on published practice guidance (Taylor, 1991). The dynamics of base cation release from fertilisers are not considered because the SMB approach works on a rotation length timeframe.

(vi) The uptake of calcium by the harvesting and removal of trees is incorporated into the SMB equation (Hall et al, 2003). For managed broadleaved woodland on mineral soils different uptake values are applied according to whether the soil type is considered to be calcium-rich or calcium-poor. For managed broadleaved woodland occurring on organo-mineral soils, the calcium uptake value for calcium-poor soils only has been applied, on the basis that the majority of upland soils are calcium-poor.

(vii) The total calcium deposition used in the SMB equation based on the molar Ca:Al ratio was updated to the latest data for 1998-2000.

(viii) The calcium weathering rates for mineral soils in Scotland were updated because the NFC discovered an error in the calculation of these values. The impacts of this change on the critical load values were assessed in November 2003 and Defra, the Devolved Administrations and data users informed. For approximately 80% of the woodland grid squares on mineral soils in Scotland the critical load was reduced by <= 0.2 keq ha^{-1} $year^{-1}$.

A summary of the methods used for the 2004 data submission is given in table 3.2.

The effect of the above changes to the methods and data used to calculate acidity critical loads for the woodland habitats have been examined (Tables 3.3 and 3.4). The changes observed are largely due to the following:

(i) For woodland on mineral soils the updated calcium deposition has led to small increases and decreases in the critical load values.

(ii) For woodland on organo-mineral soils the change in the critical chemical criterion has led to changes in the critical load values. The SMB equation based on a Ca:Al ratio is sensitive to base cation weathering (ANC_w) and the SMB equation based on critical pH is also sensitive to ANC_w, but additionally to runoff. Therefore changing the criterion has led to both increases and decreases in the critical load values due to the interactions between ANC_w and runoff in the SMB equation:

- In areas with high runoff, critical loads based on Ca:Al tend to be lower than those based on critical pH irrespective of the ANC_w value.
- Where ANC_w is low and runoff is low, critical loads based on Ca:Al tend to be lower than those based on critical pH
- Where ANC_w is medium/high and runoff is low critical loads based on Ca:Al tend to be higher than those based on critical pH

(iii) The inclusion of base cation inputs from phosphate and potassium fertilisers for managed woodlands on organic or peat soils increases the critical loads, especially for peat soils where the additions of fertiliser are greater.
(iv) The change in the definition of areas of fenland/arable peat has led to a reduction in the number of 1km squares with a critical load value of 4.0 keq ha^{-1} $year^{-1}$; the critical load values for squares no longer considered to be fenland/arable peat are lower.

A comparison of the 2003 and 2004 minimum, maximum and mean critical load values by woodland type and soil type is given in Table 3.4. The updated maps are shown in Figure 3.2. The effects of these changes in critical load values on exceedances will be discussed in an Addendum to this report to be published in April 2004.

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Table 3.1. Critical load methods and parameters applied to different soil types for CCE data submission February 2003

Soil type	**Habitat type**			
	Woodland			**Non-woodland**
	Managed conifer	**Managed broadleaf**	**Unmanaged**	
Mineral	SMB equation Ca:Al = 1 Kgibb = 950 m^6 eq^{-2} Ca uptake = 0.16 keq ha^{-1} $year^{-1}$ Total Ca deposition for 2000	SMB equation Ca:Al = 1 Kgibb = 950 m^6 eq^{-2} Ca uptake: Ca-poor soils = 0.195 keq ha^{-1} $year^{-1}$ Ca-rich soils = 0.29 keq ha^{-1} $year^{-1}$ Total Ca deposition for 2000	SMB equation Ca:Al = 1 Kgibb = 950 m^6 eq^{-2} Ca uptake = zero (assumes no harvest/removal of trees) Total Ca deposition for 2000	Empirical acidity critical loads for soils (critical loads assigned according to mineralogy & weathering rate of dominant soil in 1km grid square)
Organo-mineral	SMB equation Critical soil solution pH 4.0 ($CLA = ANC_w + (Al_{le(crit)} + H_{le(crit)})$) Kgibb = 9.5 m^6 eq^{-2} Total Ca deposition for 2000	SMB equation Critical soil solution pH 4.0 ($CLA = ANC_w + (Al_{le(crit)} + H_{le(crit)})$) Kgibb = 9.5 m^6 eq^{-2} Total Ca deposition for 2000	SMB equation Critical soil solution pH 4.0 ($CLA = ANC_w + (Al_{le(crit)} + H_{le(crit)})$) Kgibb = 9.5 m^6 eq^{-2} Total Ca deposition for 2000	Empirical acidity critical loads for soils (critical loads assigned according to mineralogy & weathering rate of dominant soil in 1km grid square)
Peat	Effective rain pH 4.4 ie, $CLA = H_{le(crit)}$ ANC_w & $Al_{le(crit)}$ set to zero CLA = 4.0 keq ha^{-1} $year^{-1}$ for any squares containing any area of arable land	Effective rain pH 4.4 ie, $CLA = H_{le(crit)}$ ANC_w & $Al_{le(crit)}$ set to zero CLA = 4.0 keq ha^{-1} $year^{-1}$ for any squares containing any area of arable land	Effective rain pH 4.4 ie, $CLA = H_{le(crit)}$ ANC_w & $Al_{le(crit)}$ set to zero CLA = 4.0 keq ha^{-1} $year^{-1}$ for any squares containing any area of arable land	Effective rain pH 4.4 ie, $CLA = H_{le(crit)}$ ANC_w & $Al_{le(crit)}$ set to zero CLA = 4.0 keq ha^{-1} $year^{-1}$ for any squares containing any area of arable land

Table 3.2 Critical load methods and parameters applied to different soil types for CCE data submission March 2004. Text in red denotes change from February 2003 submission.

Soil type	**Habitat**			
	Woodland			**Non-woodland**
	Managed conifer	**Managed broadleaf**	**Unmanaged**	
Mineral	SMB equation Ca:Al = 1 Kgibb = 950 m^6 eq^{-2} Ca uptake = 0.16 keq ha^{-1} $year^{-1}$ Total Ca deposition for 1998-2000	SMB equation Ca:Al = 1 Kgibb = 950 m^6 eq^{-2} Ca uptake: Ca-poor soils = 0.195 keq ha^{-1} $year^{-1}$ Ca-rich soils = 0.29 keq ha^{-1} $year^{-1}$ Total Ca deposition for 1998-2000	SMB equation Ca:Al = 1 Kgibb = 950 m^6 eq^{-2} Ca uptake = zero (assumes no harvest/removal of trees) Total Ca deposition for 1998-2000	Empirical acidity critical loads for soils (critical loads assigned according to mineralogy & weathering rate of dominant soil in 1km grid square)
Organo-mineral	SMB equation Ca:Al = 1 Kgibb = 100 m^6 eq^{-2} Ca uptake = 0.16 keq ha^{-1} $year^{-1}$ Total Ca deposition for 1998-2000 Include rock phosphate = 0.177 keq ha^{-1} $year^{-1}$	SMB equation Ca:Al = 1 Kgibb = 100 m^6 eq^{-2} Ca uptake = 0.195 keq ha^{-1} $year^{-1}$ (assuming all organo-mineral soils Ca-poor) Total Ca deposition for 1998-2000 Include rock phosphate = 0.08 keq ha^{-1} $year^{-1}$	SMB equation Ca:Al = 1 Kgibb = 100 m^6 eq^{-2} Ca uptake = zero (no harvest/removal of trees) Total Ca deposition for 1998-2000	Empirical acidity critical loads for soils (critical loads assigned according to mineralogy & weathering rate of dominant soil in 1km grid square)
Peat	SMB equation Critical soil solution pH 4.4 ie, CLA = $H_{le(crit)}$ ANC_w & $Al_{le(crit)}$ set to zero Include rock phosphate = 0.417 keq ha^{-1} $year^{-1}$ CLA = 4.0 keq ha^{-1} $year^{-1}$ for squares dominated by peat soil and by arable land	SMB equation Critical soil solution pH 4.4 ie, CLA = $H_{le(crit)}$ ANC_w & $Al_{le(crit)}$ set to zero Include rock phosphate = 0.417 keq ha^{-1} $year^{-1}$ CLA = 4.0 keq ha^{-1} $year^{-1}$ for squares dominated by peat soil and by arable land	SMB equation Critical soil solution pH 4.4 ie, CLA = $H_{le(crit)}$ ANC_w & $Al_{le(crit)}$ set to zero CLA = 4.0 keq ha^{-1} $year^{-1}$ for squares dominated by peat soil and by arable land	SMB equation Critical soil solution pH 4.4 ie, CLA = $H_{le(crit)}$ ANC_w & $Al_{le(crit)}$ set to zero CLA = 4.0 keq ha^{-1} $year^{-1}$ for squares dominated by peat soil and by arable land

Table 3.3. Summary of changes in critical load values for UK woodland habitats: February 2003 data submission and March 2004 data submission.

Woodland habitat	**Soil type**	**Number and percentage of 1km squares where critical load values for 2003 and 2004 are:**		
		the same	**2004 > 2003**	**2004 < 2003**
Managed coniferous	Mineral	13173 (41.8%)	3989 (12.5%)	14407 (45.7%)
	Organo-mineral	0	3478 (33.5%)	6913 (66.5%)
	Peat	27 (0.9%)	2147 (72.1%)	803 (27.0%)
Managed broadleaved	Mineral	38842 (50.4%)	9479 (12.3%)	28709 (37.3%)
	Organo-mineral	0	1424 (21.3%)	5263 (78.7%)
	Peat	Habitat no longer mapped on peat soils		
Unmanaged	Mineral	15691 (44.1%)	4511 (12.7%)	15365 (43.2%)
	Organo-mineral	0	2525 (58.5%)	1792 (41.5%)
	Peat	276 (53.6%)	0	239 (46.4%)

Refer to the text in Section 3.3 for the reasons for the changes observed in the critical loads values.

Table 3.4. Minimum, maximum and mean critical load values by woodland and soil type: comparing 2003 and 2004 values.

Woodland habitat	**Soil type**	**Critical load values (keq ha^{-1} year^{-1}) :**					
		2003 minimum	**2004 minimum**	**2003 maximum**	**2004 maximum**	**2003 mean**	**2004 mean**
Managed coniferous	Mineral	0.10	0.10	11.58	11.56	2.20	2.19
	Organo-mineral	0.27	0.28	6.50	13.44	1.66	1.58
	Peat	0.10	0.46	4.00	4.00	1.43	0.85
	All soils	0.10	0.10	11.58	13.44	2.03	1.94
Managed broadleaved	Mineral	0.10	0.10	11.71	11.68	2.91	2.91
	Organo-mineral	0.23	0.18	6.26	13.05	1.63	1.36
	Peat	0.06	Not mapped	4.00	Not mapped	2.38	Not mapped
	All soils	0.06	0.10	11.71	13.05	2.81	2.78
Unmanaged	Mineral	0.42	0.42	12.14	12.11	3.20	3.19
	Organo-mineral	0.28	0.56	5.81	12.68	1.82	1.94
	Peat	0.15	0.07	4.00	4.00	2.07	0.33
	All soils	0.15	0.07	12.14	12.68	3.04	3.02

4. ACIDITY CRITICAL LOADS FUNCTION FOR TERRESTRIAL HABITATS

4.1 Introduction

Deposition of both sulphur and nitrogen compounds can contribute to exceedance of the acidity critical load. The Critical Load Function (CLF), developed under the UNECE CLRTAP (Posch et al, 1999; Posch & Hettelingh, 1997; Posch et al, 1995; Hettelingh et al, 1995) defines combinations of sulphur and nitrogen deposition that will not cause harmful effects. The CLF is a three-node line graph representing the acidity critical load (Figure 4.1). The intercepts of the CLF on the sulphur and nitrogen axes define the "maximum" critical loads of sulphur and nitrogen. The maximum critical load of sulphur ($CL_{max}S$) is the critical load of acidity expressed in terms of sulphur only, ie, when nitrogen deposition is zero. Similarly, the maximum critical load of nitrogen ($CL_{max}N$) is the critical load of acidity in terms of nitrogen only (when sulphur deposition is zero). The long-term nitrogen removal processes in the soil (eg, nitrogen uptake and immobilisation) define a "minimum" critical load of nitrogen ($CL_{min}N$).

Combinations of deposition above the CLF would exceed the critical load, while all areas on or below the CLF line represent an "envelope of protection" where critical loads are not exceeded.

4.2 The maximum critical load of sulphur ($CL_{max}S$)

$CL_{max}S$ is based on the acidity critical load values (Chapter 3) but also takes into account the base cation deposition to the soil system and base cation removal from the system:

$$CL_{max}S = CL(A) + BC_{dep} - BC_u$$

Where $CL(A)$ = acidity critical load (empirical or SMB)
BC_{dep} = non-marine base cation less non-marine chloride deposition
BC_u = base cation removal and uptake by vegetation

The values for $CL_{max}S$ have been updated as follows:

- For the terrestrial habitats revisions have been made to the areas identified as fenland peats (Section 3.2.1) and hence the 1km grid squares with the acidity critical load set to 4.0 keq ha^{-1} $year^{-1}$.
- For the woodland habitats modifications have been made to the SMB equations used to calculate acidity critical loads (Section 3.3).
- The BC_{dep} term has been updated using 1998-2000 mean deposition values for moorland and for woodland.

The updated maps of $CL_{max}S$ for the woodland habitats are shown in Figure 4.2.

4.3 The minimum critical load of nitrogen ($CL_{min}N$)

$CL_{min}N$ is calculated as:

$$CL_{min}N = N_u + N_i + N_{de}$$

Where N_u = nitrogen removal and uptake by vegetation
N_i = nitrogen immobilisation
N_{de} = denitrification

No changes have been made to the inputs or calculation of $CL_{min}N$ for this data submission.

4.4 The maximum critical load of nitrogen ($CL_{max}N$)

$CL_{max}N$ is calculated as:

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

Changes have been made to the values of $CL_{max}N$ as a consequence of the changes to $CL_{max}S$ described above (Section 4.2). The updated woodland habitat maps of $CL_{max}N$ are shown in Figure 4.3.

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5. CRITICAL LOADS OF ACIDITY FOR FRESHWATERS

5.1 Introduction

In the 2004 update there have been two main changes to the UK critical loads of acidity for freshwaters. First, the number of freshwater sites in acidified regions for which critical loads are calculated has been increased using new survey information. Second, the value of the critical chemical threshold acid neutralising capacity (ANC) has been changed from zero to 20μeql^{-1} for all sites, except for naturally acidic sites where a value of ANC 0μeql^{-1} has been retained.

The exceedances based on the updated critical loads will be summarised in an Addendum to this report to be published in April 2004.

5.2 Updates to mapping dataset

The 2004 CCE call for data to update national acidity critical loads datasets differs from previous calls for data in that there is a move towards rationalising static (critical load) and dynamic modelling sites included in the submission. Dynamic modelling is described in Chapter 7. For consistency between static and dynamic model data submissions to the CCE mapping programme, sites for which dynamic modelling outputs are submitted must also be included in the critical loads dataset calculated using the First-order Acidity Balance (FAB) model. For this reason the UK critical loads mapping dataset has been updated to incorporate data from other studies and MAGIC model applications. In many cases, multiple samples or time series exist for mapping sites at which critical loads have previously been based on a single sample taken for the original mapping programme. In many other cases, new sites have been added to the mapping dataset for which data were previously unavailable.

The additional datasets contributing to the 2004 freshwaters critical loads submission for the UK are listed in Table 5.1.

Since many of the datasets overlap in terms of sites sampled, consistent criteria had to be employed in the selection of the chemistry data used for the calculation of critical loads. The most recent, best estimate of annual mean chemistry data were selected where multiple datasets for a site were available. The quality of the chemistry data took precedence over the sampling date, e.g. annual mean chemistry based on monthly samples for 1995 would be used in preference to one-off water samples from 1998.

5.3 Seasalts screening

The presence of exceeded sites in north-west Scotland in 2010 using an ANC_{crit} value of 20 μeql^{-1} drew attention to the problem of seasalt induced acidity in certain sites that was not distinguishable in the critical load models from anthropogenic acidity. Hence to maintain the rigour of data screening and quality assurance, a screening criterion bases on seasalt impacts was applied. All sites where the sum of non-marine

(seasalt-corrected) base cations was < -20 μeql^{-1} were removed from the mapping dataset because of the lack of confidence in calculated critical loads. It should be noted that these sites are often genuinely acid and are removed only because of the model's inability to distinguish between sources of acidification (anthropogenic deposition versus natural seasalt inputs). It cannot be said with confidence that these sites are *not* impacted by anthropogenic acid deposition.

The screening criterion led to the removal of 75 sites from the Great Britain mapping dataset, mainly in northern and north-west Scotland. No sites were screened out from the Northern Ireland dataset on this basis. The resultant mapping dataset includes 1595 sites in Great Britain and 127 sites in Northern Ireland.

5.4 Nested catchments

The amalgamation of various datasets in certain regions led to the occurrence of a number nested catchments in the mapping dataset. 118 "father" catchments were found to have one or more sub-catchments ("sons") in the mapping dataset for which ecosystem area would be double-accounted if reported separately. It was decided that only the exclusive area for the larger "father" catchments should be reported for calculation of ecosystem area exceeded (accumulated exceedance, AE). Hence the exclusive area was calculated as the difference between the total area of the father catchment and the area of the separately submitted ("son") sub-catchment. Where more than one sub-catchment occurred, the sum of sub-catchment areas was subtracted from that of the father catchment.

5.5 Stakeholder review of ANC_{crit}

As suggested in the 2003 submission report (Hall *et al.*, 2003), a stakeholder workshop was held prior to the 2004 data submission to discuss and agree the most appropriate value(s) of ANC_{crit} to be applied in the calculation of acidity critical loads for UK freshwaters. The workshop was hosted by Defra at Ashdown House, London on 27th February 2004. A summary report of the workshop is given in Appendix 2; the report outlines the options discussed and the supporting scientific evidence. The workshop concluded that an ANC_{crit} value of 20μeql^{-1} should be applied to all sites, except those where site-specific data suggest that the pre-industrial value was lower, in which case ANC_{crit} 0μeql^{-1} should be used. For the mapping dataset, the criteria for the use of ANC_{crit} = 0 μeql^{-1} include any one of the following:

1. palaeolimnological reconstruction of pH in 1850 equates to an ANC value of less than 20 μeql^{-1} for a site;
2. MAGIC model hindcast for a site indicates an ANC in 1850 of < 20μeql^{-1};
3. FAB model critical loads calculated using ANC_{crit} = 20 μeql^{-1} return a zero value, suggesting that the pre-industrial ANC value was never this low.

5.6 Updates to parameters in the First-order Acidity Balance (FAB) model

5.6.1 Adoption of new version of FAB

For the 2004 critical loads submission, the reformulated FAB model of Henriksen & Posch (2001) was applied. This version of FAB takes account of direct deposition to the lake surface, whereas the previous version (Posch *et al.*, 1997) assumed that all deposited N had first to pass through the terrestrial catchment before reaching surface waters.

The key difference between the two formulations is in the interpretation of $CL_{min}N$. In the previous version of FAB, $CL_{min}N$ represented the level of deposition at the first point of nitrate leaching into waters, so that below this deposition load, N did not contribute to critical load exceedance. In the new formulation, for lake catchments there is always some flux of N into surface waters via direct deposition. Since in-lake retention is a first-order term and a fixed proportion of inputs to the lake, there must always be a flux of nitrate from the lake outflow that contributes to a decline in ANC. In this case, $CL_{min}N$ simply represents the first point of terrestrial nitrate leaching that increases the N load to the lake and increases exceedance when the critical threshold is crossed. Hence there is no longer a category in the Critical Load Function corresponding to "reduce S deposition only" for exceeded sites; exceedance must always be due to a combination of S and N deposition where both are non-zero.

Note that in the published reformulation of Henriksen and Posch (2001), three possible scenarios of N deposition and leaching are envisaged and these are utilized in the published equations for the parameters of the Critical Load Function:

i) no terrestrial N leaching: $N_{dep} < (N_{imm}+N_{den})$

ii) terrestrial N leaching except from forested areas:

$$(N_{imm}+N_{den}) < N_{dep} < (N_{imm}+N_{den}+N_{upt})$$

iii) terrestrial N leaching from all areas:

$$N_{dep} > (N_{imm}+N_{den}+N_{upt})$$

The second case may underutilize the potential sink for N in forests by assuming that the only N input to forested areas is via direct deposition. However, if N leaching occurs from moorland areas within a catchment that are upslope of forested areas, there may be further scope for uptake of N beyond that which is directly deposited (i.e. in case ii). Hence the existing formulation provides a "worst-case" nitrate leaching scenario for forested catchments. For the UK application of FAB we have therefore modified the published equations to assume that the terrestrial N sink including forest uptake is averaged over the whole terrestrial catchment. Although this is a "best-case" nitrate leaching scenario for forested catchments, it is more consistent with the approach taken in FAB for modelling soil-based sinks for N, where the whole-catchment value for N_{imm} and N_{den} is the catchment-weighted mean for all soils.

Under this adaptation of FAB there are only two possible scenarios for N deposition and leaching. The corresponding critical load equations are given below. Note that for stream catchments where direct deposition to the water surface is negligible, the equations remain the same as in the previous formulation of FAB.

The equation for $CL_{min}N$ remains the same – only the interpretation of it changes:

$$\mathbf{CL_{min}N = (1-r)\ (N_{imm} + N_{den}) + fN_{upt}}$$

<u>Case 1: N_{dep} <= $CL_{min}N$ (no terrestrial nitrate leaching)</u>

$$CL(A) = (1-\rho_S)S_{dep} + r(1-\rho_N)N_{dep}$$

$$CL_{max}S = L_{crit} /\ (1-\rho_S)$$

$$CL_{max}N = L_{crit} /\ r(1-\rho_N)$$

<u>Case 2: N_{dep} > $CL_{min}N$ (terrestrial nitrate leaching occurs)</u>

With terrestrial N leaching the critical loads for S and N become:

$$CL(A) = (1-\rho_S)S_{dep} + (1-\rho_N)N_{dep} - (1-\rho_N)\ \{(1-r)\ (N_{imm} + N_{den}) + fN_{upt}\}$$

$$CL_{max}S = L_{crit} /\ (1-\rho_S)$$

$$CL_{max}N = (L_{crit}/(1-\rho N)) + CL_{min}N$$

The equations used for $CL_{max}S$ and $CL_{max}N$ are therefore dependent on deposition load relative to $CL_{min}N$.

The updated maps of $CL_{max}S$, $CL_{min}N$ and $CL_{max}N$ are shown in Figure 5.1.

5.6.2 Updated forestry data

Chapter 2 describes the updates made to the national habitat maps for managed coniferous and managed broadleaved woodland. These updated woodland area data resulted in minor changes to the forest cover distributions in some catchments and the new data were used in this 2004 application of FAB.

FAB incorporates the uptake of nitrogen by harvesting and removal of trees. The uptake values applied remain unchanged from February 2003: for managed coniferous woodland a net uptake rate of 0.21 keq ha^{-1} yr^{-1} (5.88 kgN ha^{-1} yr^{-1}) was used, while for managed broadleaved woodland the rate was 0.42 keq ha^{-1} yr^{-1} (2.94 kgN ha^{-1} yr^{-1}).

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Posch, M., Kämäri, J., Forsius, M., Henriksen, A. & Wilander. A. 1997. Exceedance of critical loads for lakes in Finland, Norway and Sweden: Reduction requirements for acidifying nitrogen and sulfur deposition. Environmental Management 21(2): 291-304.

Table 5.1. Datasets contributing to 2004 CCE freshwater critical loads data submission

Dataset	No. of sites	Streams	Lakes/ reservoirs	Chemistry used	Sampling date(s)	Selection criteria	Funding
FAB Mapping GB	1044	200	844	CLAG one-off	1990-94	10km/20km grid, FWS	DEFRA
NI 2000	119	50	69	DoE NI one-off	March 2000	10km grid: FWS	EHS, DoE NI
AWMN GB	19	8	11	Annual mean	2002	Spatial / sensitivity gradient	DEFRA
AWMN NI	4	3	1	Annual mean	2002	Spatial / sensitivity gradient	EHS, DoE NI
Seasalts	18	0	18	CLAG Annual mean	Quarterly 1992-93	Distance to sea / altitude	DEFRA
CLAG Nitrogen Network	13	0	13	CLAG 2 year mean	Monthly 1996-97	N deposition / Ca sensitivity	DEFRA
MK Snowdonia	76	0	76	Spring sample	February 1996	All in key grid squares	DEFRA
Analogue	27	0	27	CLAM one-off	Spring 2002	AWMN analogues	DEFRA
Trossachs	32	0	32	CLAM one-off	October 2002	All lochs in region	DEFRA
Southern England	35	0	35	CLAM one-off	September 2002	All sensitive sites in 2 regions	DEFRA
Conservation	29	0	29	CLAM one-off	Sept/Oct 2002	Random lakes in SACs	DEFRA
Pennines	64	0	64	One-off / quarterly mean	April 1998 / 2002	Most reservoirs in region	DEFRA / CEH / GANE
GANE Snowdonia	25	0	25	Quarterly mean	2002	Remote, high altitude	NERC GANE
GANE Mournes (NI)	8	0	8	Quarterly mean	2002	All in region	NERC GANE
Galloway 1998 / GANE	61	0	61	3 years 1-off / Quart. mean	1996/7/8 or 2002	Most in region	SEERAD / NERC GANE
Cairngorms	38	0	38	One-off	April-June 1999	Most in region	SEERAD
Lake District	53	0	53	One-off	May 2000	Most in region	DEFRA / CEH
WAWS lakes	16	0	16	Annual mean	Monthly 1995	Most sensitive areas: FWS	CCW/EA/Welsh Office
WAWS streams	102	102	0	Annual mean	Monthly 1995	Most sensitive areas: FWS	CCW/EA/Welsh Office
Scottish Random Survey	135	0	135	One-off	Winter 1995/96	Random subsample	NIVA/FRS-FL/ECRC
Welsh Random Survey	52	0	52	CLAM one-off	Nov/Dec 1995	Random subsample	NIVA/FRS-FL/ECRC

AWMN: UK Acid Waters Monitoring Network
CLAG: DoE/DETR Critical Loads Advisory Group
CLAM: DEFRA Freshwaters Umbrella (Critical Loads of Acidity and Metals)
FWS: Freshwater Sensitivity Map based on soils and geology (Hornung *et al.*, 1995)

6. CRITICAL LOADS OF NUTRIENT NITROGEN

No changes have been made to the methods or calculation of critical loads for nutrient nitrogen for this update.

7. DYNAMIC MODELLING

7.1 Introduction

The critical loads described in the earlier chapters are steady-state critical loads derived from static models that assume systems are in steady-state condition, in which the chemical and biological response to a change in deposition is complete. These static models do not tell us when or if the systems have reached steady-state, whereas dynamic models attempt to estimate the time required for a new state to be achieved. Just as the damage to biota was delayed beyond the onset of acid deposition, so the recovery from acidification will also be delayed. In the chain of events from the deposition of strong acids to the damage to key indicator organisms there are two major factors that can give rise to time delays. Biogeochemical processes can delay the chemical response in the catchment soils and consequently surface waters and biological processes can further delay the response of indicator organisms, such as damage to fish.

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 (or equal to) critical loads, i.e. does not exceed critical loads, and (2) the deposition is greater than critical loads, 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, and therefore the deposition should be reduced. However, it is often assumed that acidification of soils and surface waters is fully reversible and that reducing deposition to (or below) critical loads immediately removes the risk of 'harmful effects', i.e. the chemical parameter (e.g. the [ANC]-limit) 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. The removal of the risk of further damage, however, does not necessarily imply that recovery will occur. In addition, the reaction to changes in deposition is delayed by (finite) buffers, such as the cation exchange capacity (CEC) in catchment soils. These buffers can delay the attainment of a critical chemical parameter and it might take decades or even centuries, before a (new) 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. It is also likely that the desirable or critical chemical target will be achieved prior to a new steady state and so the concept of equilibrium in the long term becomes irrelevant. Dynamic models, therefore, are needed if we wish to estimate the times involved in attaining a certain chemical state in response to given 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. [ANC]>20), it will take time before full biological recovery is achieved as a result of the dispersion characteristics of the species, for example. On the other hand, the possibility remains that the original biological status will not be recovered but this possibility is common to both critical load and dynamic approaches.

Dynamic models can be applied to freshwater and terrestrial ecosystems. Dynamic models can contribute to the UNECE LRTAP Convention in two important areas:

firstly, they can provide an estimate of the expected surface water chemistry at any time in the future in response to the implementation of the Gothenburg Protocol (assessment of the impact of emission reductions) and, secondly, they can be used to assist in the calculation (optimisation) of further emission reductions (input to the process of Integrated Assessment Modelling).

There are several dynamic models available, including the Very Simple Dynamic (VSD) model recently developed by the CCE. In the UK, dynamic modelling of soils and surface waters has been mainly undertaken using the MAGIC model. A formal comparison of MAGIC and VSD has shown that the two models produce comparable simulations (Evans and Reynolds, 2003). Work on the application of VSD at site specific and regional/national scale in the UK is ongoing (Evans *et al*. 2001 and CLAM2 report, unpublished. Also see Section 7.3). Within the Convention, a Joint Expert Group on Dynamic Modelling, chaired by the UK, exists to assess and advise on the use of dynamic models and their outputs.

7.2 Application of dynamic models to UK freshwaters

Dynamic model applications are to a certain extent limited by the availability of suitable data to describe the physico-chemical characteristics of surface waters and their terrestrial catchment areas, especially soil chemistry. Given this requirement, it is clear that the focus of dynamic model applications should be on areas that are considered to be acidified or acid 'sensitive'. This makes sense within the framework of the Convention since emissions across Europe are declining and will continue to decline into the foreseeable future under the Gothenburg Protocol and so the speed of recovery from acidification is the key question.

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). 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 17 year period at many sites and in many regions around the world (Cosby *et al*. 2001). Overall, the model has proven to be robust, reliable and useful in a variety of scientific and environmental management activities (Ferrier *et al*. 1995, Jenkins *et al.* 1998, Cosby *et al*, 1995, Wright *et al*. 1998).

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 of 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 of ions from the atmosphere (wet plus dry deposition; (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 specific period. The basic output from the model is a simulation of the changes in chemical concentration/fluxes through time from pre-acidification conditions to present and on into the future under some assumption of change in atmospheric deposition of S and N (Figure 7.1).

For freshwaters, the MAGIC model has been applied to 347 sites grouped into seven regions across the UK: Galloway, SW Scotland; Cairngorms, NE Scotland; Trossachs, Central Scotland; English Lake District; S Pennines, Central England; Wales and Dartmoor, SW England. These regions are defined as acid sensitive and exhibit current critical load exceedance as calculated using the FAB model (Figure 7.2). Surface waters sampled in these regions comprise lakes, headwater streams and impoundments. The representativity of the populations of all surface waters in a region varies. For example, in the Cairngorms all standing waters are sampled whereas in the Lake District only those lakes lying on acid-sensitive geology and less than 30 ha were included.

Outputs from dynamic models can be summarised and presented as a logical extension to the critical loads approach already used in the Integrated Assessment process. For example, in the same way in which the critical loads of S and N are represented as a function for input to the Integrated Assessment Models (Chapter 4), the deposition required to achieve a given chemistry within a specified time can be calculated from the dynamic models and expressed as a target load function (TLF) (Figure 7.3). At every combination of S and N deposition on the target load function, a target ANC will be reached in the specified target year. The only difference between the TLF and the critical load function (CLF) being the concept of time to reach the target chemistry since for the CLF, the time to reach the chemical target is infinite. Note that the shape of both the CLF and TLF are similar, the ‘shelf’ at low N deposition representing the long-term capability of the system to utilise N, but the TLF will always be lower than the CLF. For a target chemistry to be reached in the very long term (infinite timescale) the TLF and CLF are the same.

Clearly and implicitly, at a currently acidified site the deposition reduction required to reach a specified target within 15 years will be greater than that required to reach the same target over a longer timescale. This is because the deposition flux over the

whole period (i.e. integral under the deposition curve over time) is largely responsible for the chemistry predicted for a given year. Assuming that costs increase with greater reduction of N and S, this implies, therefore, that there is an increased cost associated with selecting a more immediate ecosystem recovery. Additionally, it is also clear that the deposition reduction required to reach a less stringent water chemistry target (for example ANC=0 ueq/l) over the same timescale will be less than for the more stringent target (for example, ANC=30 ueq/l). Again, the economic implication is that the stricter the target chemistry, the larger emission reductions required and the higher the cost. It should be noted that the slopes of the TLFs under different target years and target chemistry will vary from site to site as a function of the buffering capacity of the soils (weathering rate, soil exchangeable base cations), the deposition (historical and current) and the predicted level of future deposition.

The specification of the TLF from a dynamic model requires one further set of assumptions regarding the timing of further emission reductions. For example, the start and end years of the required reductions must be specified since any delay in emission reduction and the time period over which they are achieved will affect the position of the TLF.

In terms of achieving an optimal solution to emission reduction, therefore, key decisions must be made regarding: (i) the target chemistry required to protect the chosen biological receptor (target chemistry) (note also that this will also influence the critical load); (ii) the year in which the target chemistry is required (target year); (iii) the year in which emission reductions will start to be implemented (implementation year); and (iv) the year in which the emission reduction must be completed (completion year). Clearly, the regional TLF constructed for use by the IAM will incorporate the result of these four assumptions.

TLFs have been calculated using MAGIC model applications in Galloway and the S Pennines. The models are calibrated with best available soils, surface water and deposition chemistry data. Present day sulphur deposition is estimated from observed surface water flux and scaled to the predicted reduction for 2010 reported in the EMEP GP-NEC[1] database. Present day nitrogen deposition is taken directly from the UK 5 km deposition database for 1998-2000 and scaled to 2010 using the reductions reported in the EMEP GP-NEC database.

The model predicts an increase in N leakage into the future despite reduced N deposition as the ability of catchment soils to immobilise N decreases through time. This increased NO_3 concentration off-sets some of the recovery in ANC resulting from reduced S deposition and this accounts in part for differences in calculated TLFs for different target years (Figure 7.4).

The TLFs for the south Pennines sites are included in the March 2004 data submission to the CCE.

[1] EMEP is the UNECE body that provides deposition maps for the UNECE region. The GP-NEC database shows deposition under the Gothenburg Protocol and the National Emissions Ceiling Directive.

7.3 Methodology for UK-scale dynamic model applications to terrestrial habitats

Defra is currently funding research on dynamic modelling for terrestrial habitats. However, dynamic modelling outputs for terrestrial habitats are not included in the March 2004 data submission to the CCE.

The UK plans to apply dynamic models to all 1 km squares in the terrestrial critical loads dataset where there is potential for current damage (i.e. chemical conditions below the critical threshold for that soil and habitat class) since these are the sites at which recovery may be expected, and target loads can be calculated. However, current conditions cannot directly be inferred from critical load exceedances, since these are indicative of steady state rather than present-day conditions. Therefore, squares considered to be potentially damaged have been identified on the basis of i) past or current critical load exceedance; and ii) low buffering capacity (i.e. empirical critical load for soil <= 0.5 keq ha^{-1} $year^{-1}$). In total, approximately 30,000 1 km squares in England and Wales and approximately 60,000 1km squares in Scotland have been identified which meet these criteria. The areas for dynamic model applications in NI have not yet been determined.

To ensure consistency between methods, dynamic models will be applied based on the dominant soil and habitat classes within each 1 km square. As far as is possible the model runs will be based on the same input data used for the national critical load and exceedance calculations, i.e. water fluxes, atmospheric deposition, empirical weathering rates, long-term N sinks and vegetation uptake. However, dynamic models also require information on finite buffering processes in the soil, i.e. cation exchange and N immobilisation. The data required to model these processes include measurements of soil cation exchange capacity, exchangeable base cations, bulk density, depth, and carbon and nitrogen pools. At the national scale, estimates of default values for these parameters will be made for each of 12 major acid sensitive soil types on the basis of a survey of 180 soil samples collected from representative locations across England, Wales and Scotland. In applying models at this spatial scale, it is not possible to calibrate sites to measured soil solution chemistry, as would be done for site-specific model applications. Consequently, there is a need for estimates of the equilibrium constants that control the exchange of base cations and aluminium between the soil exchange complex and soil solution. A pilot modelling study by Evans and Reynolds (2003) indicated that default values of these exchange constants provided in the Dynamic Modelling Manual (Posch et al., 2003) were not appropriate for UK soils, so UK-specific estimates are currently being obtained by analysing cation concentations in soil solution extracted from subsamples of the soil samples collected by centrifuging, according to the method of de Vries and Leeters (2001). The validity of the parameter values obtained, and of the methodology used to apply dynamic models at the national scale, will be checked against results from site-specific, calibrated model runs, prior to calculation of Target Loads.

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APPENDIX 1

The Simple Mass Balance (SMB) equation using a critical molar Ca:Al ratio of one in soil solution as the chemical criterion. Equation applied to woodland habitats on mineral and organo-mineral soils.

NB. Base cation (BC) terms here relate to calcium only.

$CL(A) = ANC_w + RockP - ANC_{le(crit)}$

Where:

$CL(A)$	= critical loads of acidity (calculated in eq ha^{-1} $year^{-1}$) [using units given here divide $CL(A)$ by 1000 to give keq ha^{-1} $year^{-1}$]
ANC_w	= Acid Neutralising Capacity produced by weathering (eq ha^{-1} $year^{-1}$) (base cation weathering)
$RockP$	= contribution of phosphate & potassium fertilisers to the base cation budget for managed woodlands on organo-mineral soils (eq ha^{-1} $year^{-1}$), see values in Section 3.3, Table 3.2
$ANC_{le(crit)}$	= critical leaching of ANC (eq ha^{-1} $year^{-1}$) $= -Al_{le(crit)} - H_{le(crit)}$
$Al_{le(crit)}$	= critical leaching of Aluminium (eq ha^{-1} $year^{-1}$) $= ((1.5 * BC_{le}) / Ca{:}Al) * 1000$
BC_{le}	= calcium leaching (keq ha^{-1} $year^{-1}$) $= BC_a - BC_u$
BC_u	= net uptake of calcium (keq ha^{-1} $year^{-1}$) $=$ minimum (u, BC_a)
u	= calcium uptake (keq ha^{-1} $year^{-1}$), see values in Section 3.3, Table 3.2.
BC_a	= calcium availability (keq ha^{-1} $year^{-1}$) $=$ maximum $(Ca_w + Ca_{dep} - BC_{lemin}, 0)$
Ca_w	= calcium weathering (keq ha^{-1} $year^{-1}$)
Ca_{dep}	= total (marine plus non-marine) calcium deposition for woodland 1995-97 (keq ha^{-1} $year^{-1}$)
BC_{lemin}	= minimum calcium leaching (keq ha^{-1} $year^{-1}$) $Q * [BC_l] * 0.01$
Q	= runoff (metres $year^{-1}$)
$[BC_l]$	= limiting concentration for uptake of calcium (2μeq l^{-1})
$H_{le(crit)}$	= critical leaching of hydrogen ions (eq ha^{-1} $year^{-1}$) $= (1.5 * ((BC_{le} * 1000) / (K_{gibb} * Ca{:}Al)))^{1/3} * (Q * 10000)^{2/3}$
K_{gibb}	= gibbsite equilibrium constant (see values in Section 3.3, Table 3.2)
$Ca{:}Al$	= Calcium:Aluminium ratio = 1

APPENDIX 2

STAKEHOLDER REVIEW OF ANC_{CRIT}

As suggested in the 2003 submission report (Hall *et al.*, 2003), a stakeholder workshop was held prior to the 2004 data submission to discuss and agree the most appropriate value(s) of ANC_{crit} to be applied in the calculation of acidity critical loads for UK freshwaters. The workshop was hosted by Defra at Ashdown House, London on 27th February 2004.

Aims of the workshop

In the 2003 freshwaters critical load data submission to CCE, the issue of the most appropriate value of ANC_{crit} for UK fresh waters was raised in the light of new work being done within the DEFRA sponsored Freshwaters Umbrella Programme. It was suggested that the current value used for all previous UK submissions of ANC_{crit}=0 μeql^{-1} provided a very modest level of protection to many freshwater organisms and that evidence was building for a review of the critical chemical threshold. In particular, the requirements of the EU Water Framework Directive for a return to "good ecological status" and of the Habitats Directive for protection of key organisms and habitats of conservation interest may not be well served by such a low level of protection.

This workshop provided the forum for the presentation of new research and discussions with stakeholders on the weight of evidence for an increase in ANC_{crit} to a higher value of 20 μeql^{-1}, as used widely elsewhere in Europe.

The aim of the workshop was to reach a consensus on the methodology and underlying principles to update the official UK dataset for critical loads for freshwaters, taking into account recent advances in understanding of biological response to surface water acidification and recovery within the UK.

Scientific presentations

The workshop presentations and discussions centred on three themes:

1. what were the pre-industrial conditions in acid sensitive freshwaters in the UK in terms of the critical chemical parameter, ANC?
2. what biological evidence is there for responses at ANC values of 0 and 20 μeql^{-1} including evidence for recovery in waters with declining sulphate and increasing ANC?
3. what is the current state of UK freshwaters in terms of ANC and critical load exceedance?

<u>1. Baseline conditions</u>

Knowledge of pre-industrial, baseline (or reference) conditions is of great importance for setting recovery targets, for defining "good ecological status" under the WFD and crucially, for setting an appropriate value of ANC_{crit}. Two approaches have been

employed here; palaeolimnological reconstruction of water chemistry (pH and ANC) from lake sediments and dynamic modelling using MAGIC.

Palaeolimnological data for 114 lakes across the UK were collated and provide reconstructed lakewater pH from diatom-pH transfer functions for the pre-industrial baseline of 1850. While a direct transfer function for ANC is still under development, it is possible to derive ANC from reconstructed pH indirectly using relationships found in modern water chemistry. It was concluded that the great majority of sites would have had a pre-industrial ANC of > 20 μeql^{-1}, in many cases much higher. In a small number of sites, pre-industrial ANC could have been lower than 20 μeql^{-1}, but always greater than 0 μeql^{-1}.

Regional applications of the MAGIC model provided hindcast ANC distributions for lake populations in several key regions impacted by acidification; Wales, the South Pennines, the Lake District, Galloway, the Cairngorms and the Mourne Mountains of Northern Ireland. In Wales and Galloway, no lakes had a modelled ANC below 20 μeql^{-1} in 1850. In the other regions a very small number of sites had modelled pre-industrial ANC values in the range 0-20 μeql^{-1} while the great majority had values >20 μeql^{-1}.

2. Biological evidence

A chemical-biological database collated specifically for the purpose provided evidence of more acid-sensitive elements of the biota than the widely used indicator species, brown trout. Several invertebrate species including the mayfly *Baetis rhodani*, as well as the diatom *Achnanthes minutissima*, rarely occur in waters with a mean ANC of <20 μeql^{-1}. Even brown trout in the Welsh Acid Waters Survey were found to be largely absent in streams with mean ANC <20 μeql^{-1}. Experimental work in Wales and elsewhere has demonstrated that invertebrate populations may be impacted more by minimum pH and ANC values during acid episodes in streams so that mean water chemistry is a poor predictor of biological status. A lower level of protection is therefore afforded to invertebrates in streams than in lakes for a given mean value of ANC, requiring a higher value of ANC_{crit} for streams to provide an equivalent level of protection as for lakes.

Data from the UK Acid Waters Monitoring Network (AWMN) show chemical recovery in surface waters in response to declining sulphur deposition since 1995, with sulphate concentrations decreasing and a corresponding increase in ANC in many sites. Early signs of biological recovery are also apparent, especially in diatom communities and subtle changes in invertebrate communities. In a number of sites, elodeid macrophytes have re-appeared where ANC has increased above the range 15-20 μeql^{-1}, suggesting a possible recovery threshold.

3. Current status of UK freshwaters and effects of ANC_{crit} on critical load exceedance

The critical load exceedance results will be added at the end of March.

Summary of new data

All the evidence from palaeolimnological, static and dynamic models suggests that the great majority of surface waters in the UK had a pre-industrial ANC of >20 μeql^{-1}.

Biological data suggest that a number of organisms may be adversely affected when mean ANC declines to 0 μeql^{-1} but an increase from 0 to 20 μeql^{-1} represents a major improvement in biological status. Hence ANC_{crit} = 20 μeql^{-1} may reasonably be considered to provide a defensible threshold for acidity.

It is recognised that in a small number of sites, pre-industrial ANC may have been less than 20 μeql^{-1} (but greater than 0 μeql^{-1}) and in such cases ANC_{crit} = 20 μeql^{-1} provides an unachievable critical load.

Discussion and agreement of new ANC_{crit}

In the context of the research findings presented above, several options for updating the value of ANC_{crit} employed in the 2004 critical loads submission to CCE were considered.

1. Blanket value of ANC_{crit} = 0 μeql^{-1} (as used in the February 2003 update)
The workshop considered that the weight of evidence no longer supported the blanket use of ANC_{crit} = 0 μeql^{-1} for the UK, given the relatively high probability of damage allowed and the large distance from "good ecological status" implied.

2. Blanket value of ANC_{crit} = 20 μeql^{-1}
A blanket value of ANC_{crit} = 20 μeql^{-1} is inappropriate because a small number of sites that may not have had a pre-industrial ANC as high as 20 μeql^{-1}.

3. ANC_{crit} = 20 μeql^{-1} for streams and 0 μeql^{-1} for lakes
While the data suggest that ANC_{crit} = 20 μeql^{-1} should be a minimum value for streams the continued use of 0 μeql^{-1} for lakes was deemed inappropriate as providing too low a level of protection (see 1 above).

4. ANC_{crit} = 20 μeql^{-1} with exceptions at 0 μeql^{-1}
The workshop agreed that this option provides a pragmatic and widely acceptable solution, with a more appropriate level of protection for all sites. Where site-specific modelling work suggests than an ANC of 20 μeql^{-1} is unattainable through emissions reductions because of a lower pre-industrial (reference) value, then the lower threshold of 0 μeql^{-1} should be used, ie, naturally acid sites retain a value of 0 μeql^{-1}.

5. Site-specific ANC_{crit}, using reference conditions and/or specific indicator species
While this option provides the optimal level of protection appropriate for each site, the necessary data are lacking for a large proportion of sites in the mapping dataset, so there are great practical limitations to its application. However, for site-specific assessments at individual sites of high conservation or amenity value, this option is the most appropriate.

6. Assign ANC_{crit} according to typology
The requirement to assign typologies to surface waters under the EU Water Framework Directive (WFD) would suggest that ANC_{crit} based on typologies may bring critical loads modelling into line with WFD approaches. However, it was agreed

that typology definitions were currently too broad and poorly defined to make this option feasible at present.

Conclusion

The workshop supported the adoption of Option 4 – a general ANC_{crit} value of 20 μeql^{-1} except where site-specific data suggest that the pre-industrial value was lower, in which case $ANC_{crit} = 0\ \mu eql^{-1}$ should be used.

For the mapping dataset, the criteria for the use of $ANC_{crit} = 0\ \mu eql^{-1}$ include any one of the following:

4. palaeolimnological reconstruction of pH in 1850 equates to an ANC value of less than 20 μeql^{-1} for a site;
5. MAGIC model hindcast for a site indicates an ANC in 1850 of < 20μeql^{-1};
6. FAB model critical loads calculated using $ANC_{crit} = 20\ \mu eql^{-1}$ return a zero value, suggesting that the pre-industrial ANC value was never this low.

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