**Research Article**

# Acidification in European mountain lake districts: A regional assessment of critical load exceedance

**Chris J. Curtis[1],\*, Ivan Botev[2], Lluis Camarero[3], Jordi Catalan[3], Dan Cogalniceanu[4], Mike Hughes[1], Martin Kernan[1], Jiří Kopáček[5], Atte Korhola[6], Roland Psenner[7], Michela Rogora[8], Evžen Stuchlík[9], Mauro Veronesi[10] and Richard F. Wright[11]**

[1] Environmental Change Research Centre, 26 Bedford Way, London WC1H 0AP, United Kingdom

[2] Institute of Zoology, Bulgarian Academy of Sciences, Boul.Tsar Osvoboditel 1, 1000 Sofia, Bulgaria

[3] Limnology Group, CEAB-CSIC, Acces Cala St. Francesc 14, Blanes 17300, Spain

[4] Dept. of Ecology, Bucharest University, Splaiul Independentai 91–95, 76201 Bucharest, Romania

[5] Czech Rep. Academy of Sciences, Na sadkach 7, Ceske Budejovice, CZ-370 05, Czech Republic

[6] Dept. of Biological and Environmental Sciences, Division of Aquatic Sciences / ECRU, University of Helsinki, P.O. Box 65 (Viikinkaari 1), FIN-00014, Finland

[7] Inst. of Zool. and Limnology, University of Innsbruck, Technikerstr. 25, A-6020 Innsbruck, Austria

[8] C.N.R. Institute of Ecosystem Study, Largo Tonolli 50–52, I-28922 Verbania Pallanza, Italy

[9] Charles University, Vinicna 7, Prague, CZ-128 44, Czech Republic

[10] Uff. Protezione e Depurazione Acque-SPAAS, Riva Paradiso 15, CH-6900 Paradiso-Lugano, Switzerland

[11] Norway Institute for Water Research, P.O. Box 173, Kjelsaas N-0411 Oslo, Norway

**Abstract.** High mountain lakes are sensitive to environmental change and the effects of air pollution and lake acidification have been recorded in many countries. The EU funded EMERGE programme included a pan-European assessment of the extent of acidification in mountain lakes located above the tree-line. A static critical loads model, the First-order Acidity Balance (FAB) model, was used to assess (1) the extent of critical load exceedance in 300 lakes in nine European lake districts and (2) the relative importance of sulphur and nitrogen deposition in contributing to acidification. The regional sensitivity of FAB to the choice of critical acid neutralising capacity (ANC: 0 or 20 µeq $L^{-1}$) was explored. With a critical ANC value of 0 µeq $L^{-1}$ only four lake districts had sites showing exceedance of critical loads; Piedmont Ticino, the Pyrenees, the Retezat Mountains and the Tatras. When a more stringent critical ANC of 20 µeq $L^{-1}$ was used, all nine lake districts showed critical load exceedance in one or more lakes. For two lake districts, the Retezat Mountains of Romania and the Rila Mountains of Bulgaria, critical load exceedance is recorded here for the first time. Nitrogen is a more important agent of acidification in some areas such as the Pyrenees and Piedmont Ticino, and its relative importance is likely to increase elsewhere as pan-European measures to reduce sulphur deposition continue to take effect. Given the coarse scale deposition data used and potentially underestimated loads at high altitudes, the extent of the acidification problem may be under-represented here.

**Key words.** FAB model; sulphur; nitrogen; EMERGE; regionalisation; alpine lakes.

**\*** Corresponding author phone: +44-207-679-7553; fax: +44-207-679-7565; e-mail: ccurtis@geog.ucl.ac.uk

## Introduction

Remote mountain lakes, by virtue of their inaccessibility and distance from human activities, are relatively unpolluted systems compared with lowland lakes, and often affected only by long-range transported atmospheric pollutants. However, even the low pollutant levels experienced by most sensitive mountain lakes cause measurable change in lakewater chemistry and biology, to the extent that in some mountain regions these lakes are far from pristine (Grimalt et al., 2001; Skjelkvåle and Wright, 1998). A well-known phenomenon is that of surface water acidification in areas of base-poor soils and crystalline geology, which are frequently coincident with mountainous regions of slow-weathering, igneous rocks. Local and regional studies have found widespread evidence of mountain lake acidification, ranging from subtle long-term changes predicted by critical loads models (Marchetto et al., 1994; Boggero et al., 1998; Curtis et al., 2002) to severe biological damage in areas with a long history of high acid deposition loads (Kopáček et al., 2001).

Acidification status is one of the suite of water quality variables recommended for assessment under the requirements of the EU Water Framework Directive (EU, 2000). The EU funded EMERGE programme (European Mountain lake Ecosystems: Regionalisation, diagnostics and socio-economic Evaluation) provided the first opportunity to carry out a pan-European assessment of the extent of the acidification problem in a particular lake habitat assumed to be highly sensitive, that of alpine lakes, or mountain lakes located above the tree-line (hereafter "mountain lakes"). While other European scale studies of acidification have focussed on long time-series of data from lakes and streams (Evans et al., 2001; Forsius et al., 2001; Mosello et al., 2002; Stoddard et al., 1999) or focussed on Northern Europe (e.g. Henriksen et al., 1998) or Southern Europe (Camarero et al., 1995) the acidification threat to mountain lakes has never previously been assessed on a regional basis for lakes sampled over a similar period at such a broad scale. Here, we quantify the effects of anthropogenic sulphur and nitrogen deposition in 12 European mountain regions spanning 14 countries, using the First-order Acidity Balance model (FAB), an established critical loads model (Posch et al., 1997).

## Data sources and methods

Static critical loads models provide estimates of potential damage from an atmospheric pollutant (here, acid deposition) to specified elements of an ecosystem (Bull, 1991). Static models are used for freshwaters because they can use lake water chemistry to provide integrated information on catchment scale hydrochemical processes that are otherwise difficult to measure (Henriksen et al., 1992a), especially in remote mountain catchments.

The simplest static critical loads model, the steady-state water chemistry (SSWC) model (Henriksen et al., 1992a), has minimal input data requirements and can be applied to any lake with major ion water chemistry data ($Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $SO_4^{2-}$, $NO_3^-$, $Cl^-$) plus estimates of net runoff (effective precipitation) and acid deposition. Temporal variations in water chemistry are accounted for by the use of estimated annual mean fluxes of acid anions in both surface water and deposition. The SSWC model provides an estimate of the sustainable (pre-industrial) leaching rate of base cations (BC) and hence of acid neutralizing capacity (ANC) for a given deposition and leaching of acid anions (AN), with ANC defined as $\Sigma BC - \Sigma AN$ (Henriksen, 1984; Brakke et al., 1990).

The more complex FAB model (Posch et al., 1997; Henriksen and Posch, 2001) builds on the SSWC model to incorporate a mass/charge balance for nitrogen, so that potential changes in N leaching are accounted for. To estimate the N mass balance, catchment scale soils data, lake:catchment area ratio and N fluxes in biomass removed by harvesting are required. The FAB model was designed to meet the requirements of integrated assessment models (e.g. RAINS) applied at the European scale to assess the effects of deposition scenarios for both S and N deposition and hence is one of the recommended models for critical loads work at the scale of the European Monitoring and Evaluation Programme (EMEP: Posch et al., 1997; Curtis et al., 2005) under the UNECE Convention on Long Range Transboundary Air Pollution (CLRTAP).

The FAB mass balance for the lake catchment, incorporating major sources and sinks of S and N, is summarised below; for a full description of individual terms see Curtis et al. (1998):

$$N_{dep} + S_{dep} = f N_{upt} + (1-r)(N_{imm} + N_{den})$$
$$+ r N_{ret} + r S_{ret} + AN_{leach} \qquad (1)$$

$N_{dep}$ = total N deposition
$S_{dep}$ = total S deposition
$N_{upt}$ = net growth uptake of N by forest vegetation (removed by harvesting)
$N_{imm}$ = long-term immobilization of N in catchment soils
$N_{den}$ = N lost through denitrification in catchment soils
$N_{ret}$ = in-lake N retention
$S_{ret}$ = in-lake S retention
$AN_{leach}$ = leaching of acid anions (S+N) from catchment
$f$ = fraction of forested area in the catchment
$r$ = lake:catchment area ratio

(all units, except the dimensionless $f$ and $r$, are equivalents per unit area and time)

The acid anion balance of the FAB model can provide the critical leaching flux of acid anions (critical $AN_{leach}$) which will depress ANC below a pre-selected critical value ($ANC_{crit}$) as in the SSWC model (Henriksen et al., 1992a). Therefore, at critical load, $AN_{leach}$ can be substituted into Equation 1 as:

$$AN_{leach} = BC_{crit} - (ANC_{crit}) \cdot Q \qquad (2)$$

where $BC_{crit}$ is the sustainable leaching flux of base cations from weathering and fixed deposition inputs calculated according to the SSWC model, and Q is runoff, used to convert the critical ANC concentration to a flux.

Within the EMERGE programme, 353 survey lakes with catchment scale data in the 12 defined lake districts were sampled for water chemistry during the ice-free period (generally July – November 2000), with one-off surface or lake outflow samples being used for critical loads work (Table 1). Both sampling and chemical analyses were performed according to standard protocols developed in previous projects on mountain lakes, such as AL:PE 1 and 2 and MOLAR (Mosello et al., 1997; Mosello and Wathne, 1997; MOLAR Water Chemistry Group, 1999).

As part of the analytical quality control (AQC) within each national laboratory, ionic balances and comparisons of measured and calculated conductivity were used as routine checks for all the analyses performed. Data were classified according to conductivity values (above or below 25 μS cm$^{-1}$ at 25°C) and ionic balance error (Δ%), calculated as $(100*(\Sigma \text{ cations} - \Sigma \text{ anions})/(\Sigma \text{ cations} + \Sigma \text{ anions}))$. Data were accepted if Δ% was <10 or <20 for conductivity values above or below 25 μS cm$^{-1}$, respectively, with 89% of the data accepted on these criteria. All major ions were available for 94–98% of the samples and only these data were used for critical loads modelling.

While the intention was to sample across environmental gradients in each lake district, criteria for the selection of survey sites varied between districts, as did the proportion of the mountain lake population sampled (Table 1). For example, in Scotland, the mountain lake population was defined as all lochs greater than 0.5 ha in surface area above a regionally varying theoretical tree-line (n = 399), from which a subset of 30 (7.5%) were selected across gradients of altitude and geology (Helliwell and Kernan, 2004). In another lake district, the Tatra Mountains, almost three quarters of all alpine lakes were sampled to provide representative data in both spatial and morphological terms. Hence the range of physical characteristics and general representativeness of survey lakes in terms of regional populations varied greatly between lake districts. However, a study of mapped and remotely-sensed, physical catchment attributes for surveyed and unsampled lakes concluded that the physical and geological properties of survey lake catchments had very similar distributions to those of the whole mountain lake population in each lake district (Curtis et al., 2005). On this basis it was concluded that the range of chemical properties in survey lakes should be representative for the corresponding lake district populations.

S and N deposition data for 2000 were derived for lakes in the whole of the EMERGE study area except Greenland from the EMEP 50 km database (Simpson et al., 2003) by interpolation to individual sites from the nearest EMEP grid cells (Table 2). Precipitation data were derived from national datasets where possible, otherwise EMEP scale data derived in the same way as deposition were used. Runoff data were not widely available for survey sites, but unpublished hydrological budget studies at ten EMERGE survey lakes across the Pyrenees, Piedmont Ticino, Tyrol, Tatras, Scotland and southern Norway found that runoff varied from 71 to 95% of pre-

**Table 1.** Number and proportion of survey lakes, with minimum measured ANC in each lake district.

| Code | Lake District Name | Country | No. sites | % of total | Min. ANC (μeq L$^{-1}$) |
|------|--------------------|---------|-----------|-----------|--------------------------|
| CA | Central Alps | Switzerland | 12 | 25.0 | 136* |
| CN | Central Norway | Norway | 22 | 10.3 | 8 |
| JA | Julian Alps | Slovenia | 14 | 100.0 | 850 |
| NF | Northern Finland | Finland | 40 | 6.8 | 5 |
| PT | Piedmont Ticino, Alps | Italy / Switzerland | 29 | 19.7 | −7 |
| PY | Pyrenees | France / Spain | 85 | 8.0 | −224 |
| RE | Retezat Mountains, Southern Carpathians | Romania | 6 | 10.3 | 38 |
| RI | Rila Mountains, Balkans | Bulgaria | 9 | 10.7 | 31 |
| SC | Scotland | UK | 30 | 7.5 | 16 |
| SS | Greenland | Denmark | 27 | 1.5 | 800 |
| TA | Tatras, Northern Carpathians | Poland / Slovakia | 48 | 72.7 | −32 |
| TY | Tyrol, Alps | Austria / Italy | 31 | 6.7 | 8 |

* alkalinity – insufficient major ion data for independent calculation of ANC.

**Table 2.** Range and mean of lake and catchment characteristics plus FAB model parameters for modelled Lake Districts.

| Lake District | | Lake area (ha) | Catchment area (ha) | L:C ratio | Altitude (m) | Max. depth (m) | % Bare ground | % Peat | Net den. | Net N imm. | $\varrho_N$ | $\varrho_S$ | Runoff (mm) | S dep. | N dep. (keq ha⁻¹ yr⁻¹) | xSO₄²⁻ (All sites) | NO₃⁻ | xSO₄²⁻ (Exceeded*) | NO₃⁻ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CN | Min | 8.00 | 120.0 | 0.014 | 466 | 6.0 | 10 | 0 | 0.074 | 0.369 | 0.060 | 0.006 | 525 | 0.06 | 0.15 | 8.1 | 0.0 | 10.2 | 0.5 |
| | **Mean** | **76.84** | **1912.3** | **0.083** | **1078** | **18.7** | **10** | **0** | **0.083** | **0.413** | **0.279** | **0.042** | **962** | **0.12** | **0.26** | **24.0** | **1.1** | **14.7** | **2.0** |
| | Max | 180.00 | 8880.0 | 0.180 | 1525 | 40.0 | 10 | 0 | 0.089 | 0.443 | 0.506 | 0.093 | 1445 | 0.20 | 0.43 | 81.2 | 3.9 | 20.2 | 3.9 |
| NF | Min | 1.24 | 23.0 | 0.005 | 167 | 0.1 | 0 | 0 | 0.000 | 0.000 | 0.045 | 0.005 | 437 | 0.06 | 0.07 | 9.6 | 0.1 | 9.6 | 0.1 |
| | **Mean** | **24.43** | **296.3** | **0.112** | **572** | **7.5** | **43** | **0** | **0.052** | **0.250** | **0.449** | **0.090** | **575** | **0.08** | **0.07** | **36.8** | **0.2** | **10.4** | **0.4** |
| | Max | 105.88 | 1337.5 | 0.334 | 1024 | 27.0 | 100 | 9 | 0.154 | 0.487 | 0.770 | 0.251 | 845 | 0.15 | 0.08 | 123.9 | 1.4 | 12.3 | 1.4 |
| PT | Min | 0.10 | 9.1 | 0.007 | 1692 | 2.0 | 21 | 0 | 0.000 | 0.000 | 0.017 | 0.002 | 1943 | 0.36 | 1.12 | 23.8 | 1.4 | 23.8 | 8.9 |
| | **Mean** | **4.16** | **88.8** | **0.051** | **2154** | **17.1** | **84** | **0** | **0.020** | **0.098** | **0.097** | **0.011** | **2156** | **0.39** | **1.23** | **49.3** | **18.7** | **36.5** | **20.7** |
| | Max | 20.11 | 292.0 | 0.166 | 2580 | 68.0 | 100 | 0 | 0.089 | 0.445 | 0.254 | 0.033 | 2523 | 0.43 | 1.37 | 119.6 | 36.1 | 44.7 | 36.1 |
| PY | Min | 0.24 | 7.0 | 0.001 | 1620 | 0.7 | 0 | 0 | 0.000 | 0.000 | 0.007 | 0.001 | 1099 | 0.26 | 0.81 | 8.8 | 0.0 | 10.7 | 0.2 |
| | **Mean** | **8.21** | **248.3** | **0.067** | **2291** | **22.2** | **60** | **0** | **0.037** | **0.185** | **0.169** | **0.022** | **1442** | **0.36** | **1.07** | **90.4** | **6.3** | **150.8** | **6.7** |
| | Max | 53.19 | 5437.9 | 0.287 | 2990 | 123.0 | 100 | 0 | 0.099 | 0.495 | 0.512 | 0.095 | 1751 | 0.49 | 1.24 | 1239.4 | 19.9 | 1239.4 | 17.8 |
| RE | Min | 0.36 | 7.6 | 0.013 | 1920 | 1.1 | 35 | 0 | 0.024 | 0.122 | 0.045 | 0.005 | 1232 | 0.91 | 0.86 | 48.1 | 0.0 | 48.1 | 0.0 |
| | **Mean** | **2.47** | **46.5** | **0.052** | **2073** | **12.2** | **58** | **0** | **0.040** | **0.200** | **0.162** | **0.020** | **1299** | **0.91** | **0.86** | **54.9** | **14.5** | **52.2** | **13.4** |
| | Max | 6.51 | 117.8 | 0.085 | 2260 | 29.0 | 7 | 0 | 0.059 | 0.297 | 0.257 | 0.033 | 1382 | 0.91 | 0.86 | 68.6 | 24.3 | 57.0 | 24.3 |
| RI | Min | 0.70 | 11.0 | 0.008 | 2243 | 4.5 | 0 | 0 | 0.084 | 0.418 | 0.030 | 0.003 | 1319 | 0.74 | 0.66 | 44.8 | 0.0 | | |
| | **Mean** | **3.91** | **97.9** | **0.064** | **2432** | **16.8** | **0** | **0** | **0.094** | **0.468** | **0.174** | **0.023** | **1319** | **0.74** | **0.66** | **61.1** | **4.0** | **44.8** | **7.8** |
| | Max | 9.10 | 217.5 | 0.163 | 2709 | 37.5 | 0 | 0 | 0.099 | 0.496 | 0.382 | 0.058 | 1319 | 0.74 | 0.66 | 86.8 | 15.0 | | |
| SC | Min | 0.91 | 10.8 | 0.019 | 520 | 1.0 | 0 | 0 | 0.022 | 0.088 | 0.069 | 0.007 | 978 | 0.12 | 0.20 | 3.6 | 0.0 | | |
| | **Mean** | **6.50** | **76.3** | **0.093** | **679** | **13.5** | **33** | **7** | **0.111** | **0.306** | **0.213** | **0.028** | **1674** | **0.15** | **0.31** | **16.7** | **2.4** | **5.5** | **2.7** |
| | Max | 31.10 | 246.8 | 0.213 | 920 | 47.0 | 82 | 42 | 0.383 | 0.461 | 0.474 | 0.083 | 2429 | 0.20 | 0.43 | 40.9 | 13.0 | | |
| TA | Min | 0.05 | 1.6 | 0.004 | 1311 | 1.5 | 0 | 0 | 0.015 | 0.073 | 0.016 | 0.002 | 545 | 0.78 | 1.00 | 24.2 | 0.0 | 24.2 | 0.0 |
| | **Mean** | **4.63** | **82.6** | **0.061** | **1821** | **17.8** | **60** | **0** | **0.038** | **0.189** | **0.181** | **0.025** | **1202** | **0.79** | **1.01** | **43.3** | **24.5** | **36.9** | **24.6** |
| | Max | 34.54 | 630.0 | 0.332 | 2145 | 79.3 | 85 | 0 | 0.098 | 0.490 | 0.569 | 0.116 | 1384 | 0.86 | 1.07 | 96.8 | 46.5 | 47.8 | 46.5 |
| TY | Min | 0.52 | 13.9 | 0.005 | 1840 | 2.2 | 3 | 0 | 0.005 | 0.024 | 0.011 | 0.001 | 1534 | 0.18 | 0.63 | 10.3 | 0.0 | | |
| | **Mean** | **2.40** | **62.7** | **0.059** | **2380** | **11.3** | **44** | **0** | **0.053** | **0.263** | **0.121** | **0.015** | **2037** | **0.24** | **0.82** | **159.5** | **9.3** | **21.7** | **9.1** |
| | Max | 7.19 | 209.8 | 0.228 | 2796 | 44.6 | 95 | 0 | 0.095 | 0.477 | 0.393 | 0.061 | 3357 | 0.37 | 1.28 | 2206.2 | 27.1 | | |

L:C ratio: lake:catchment area ratio; Net den.: net denitrification flux (keq ha⁻¹ yr⁻¹); Net N imm.: net N immobilisation (keq ha⁻¹ yr⁻¹); $\varrho_N$: in-lake retention fraction for N; $\varrho_S$: in-lake retention fraction for S; S dep.: non-marine S deposition; N dep.: total N deposition; xSO₄²⁻: excess (non-marine) sulphate concentration in lake water (µeq L⁻¹); NO₃⁻: nitrate concentration in lake water (µeq L⁻¹); * FAB model critical load exceeded with ANC$_{crit}$ = 20 µeq L⁻¹

cipitation, with a mean for all sites of 80% (Uli Nickus, pers. comm.). Runoff was therefore assumed here to be 80% of total precipitation for all sites. Site-specific modelled precipitation data were unavailable for the Rila Mountains and the Tyrol. For these districts, a crude estimate of runoff was derived from the 50 km grid scale EMEP precipitation data for 2000 (Table 2).

For a full application of the FAB model, catchment scale information on soil type and vegetation cover is required. Basic soils data (% bare ground and % peat soils) plus catchment and lake area information were derived from GIS analysis of mapped and remotely sensed spatial data (Casals-Carrasco et al., submitted: Table 2). A key feature of mountain lakes is that a large proportion of their catchments may be made up of bare rock (where no terrestrial N sinks are available), so a correction was made in catchment weightings to account for the area of each catchment that is devoid of soil cover.

While a previous application of FAB to high mountain lakes (Curtis et al., 2002) employed values for long-term immobilisation of N in soils ($N_{imm}$) based on soil type (Hall et al., 1997), a value of 0.5 kgN ha$^{-1}$ yr$^{-1}$ was assumed here in the absence of detailed soil cover data. This value is at the bottom end of the suggested range of 0.5 – 1.0 kgN ha$^{-1}$ yr$^{-1}$ suggested in the UNECE Mapping Manual for critical loads (UBA, 1996) and was used in a previous FAB model application in Norway (Henriksen, 1998). Denitrification ($N_{den}$) is based on a linear interpolation between assumed denitrified fractions ($F_{de}$) of 80% of net inputs for peat soils and 10% for all other soils (Posch et al., 1997). In-lake retention fractions for S ($\varrho_S$) and N ($\varrho_N$) are based on a first-order equation using empirical mass-transfer coefficients, lake:catchment area ratio and runoff (Kelly et al., 1987; Dillon and Molot, 1990; Kaste and Dillon, 2003). The range and mean of calculated FAB model terms for each lake district is provided in Table 2.

The basic catchment scale soils data required for FAB model application were available for most survey lakes, but soils data were lacking for all 22 sites in Central Norway, two sites in Piedmont Ticino and one Scottish site. For sites with existing soils data the proportion of peat cover was typically very low (<5%) while the proportion of bare ground was very variable (see Table 2). Hence for the sites with missing soils data described above, peat cover was assumed to be negligible and bare ground was conservatively assumed to be 10%. These assumptions led to catchment specific figures of 0.09 (9%) for the denitrification fraction ($F_{de}$) and 0.45 keq ha$^{-1}$ yr$^{-1}$ for N immobilisation.

In the FAB model the major export term for N in harvested biomass is assumed to be from managed woodland, with grazing fluxes only important where livestock are removed from areas of intensive grazing. Within EMERGE, mountain lakes above the tree line make up the study population, so forestry and grazing removal of N ($N_{upt}$) were assumed to be negligible.

The international critical loads mapping and integrated modelling exercises undertaken under the auspices of the CLRTAP permit signatory nations to select their own critical ANC value for use in critical loads models, above which lake-water ANC must be maintained at steady-state. The lowest value has been employed in the UK (ANC$_{crit}$ = 0 µeq L$^{-1}$: Curtis et al., 2000) while other countries have used 20 µeq L$^{-1}$ (Henriksen et al., 1992a; 1998), based on well-established relationships between ANC and the health of brown trout and invertebrate populations for Norwegian lakes and rivers (Lien et al., 1996). The same value of 20 µeq L$^{-1}$ was used by Marchetto et al. (1994) on the basis of evidence that phytoplankton and zooplankton in alpine lakes may be affected at lower ANC values. While the biology of all survey lakes within the current study is not known, a critical ANC of 20 µeq L$^{-1}$ is used here to represent a level that should prevent acidification damage to many aspects of the biodiversity of mountain lakes. Since the EMERGE lake districts fall within many different countries, the model has also been applied with the lower ANC$_{crit}$ value of 0 µeq L$^{-1}$ for comparison, representing a lower level of protection against acidification effects on biodiversity. An alternative method using a regionally adapted variable ANC$_{crit}$ value (Henriksen and Posch, 2001) was not applied here because of the introduction of a further source of uncertainty in defining appropriate regional limits, while the fixed values used are better suited to inter-regional comparisons.

The FAB mass balance enables the calculation of hypothetical "individual" critical loads for either S or N deposition if it is assumed that deposition of the other is zero. For example, if the calculated leaching flux of S is greater than the critical value of AN$_{leach}$ then regardless of N deposition, S deposition must be reduced until the S leaching flux is lower than AN$_{leach}$. Reductions in S deposition are therefore compulsory to prevent critical load exceedance. Likewise, the corresponding mass balance may be calculated for N, so that if the N leaching flux exceeds AN$_{leach}$, reductions in N deposition are also compulsory to prevent critical load exceedance. The different terms in the mass balances for S and N lead to different maximum permissible deposition loads for each, termed CL$_{max}$S and CL$_{max}$N, to prevent critical load exceedance. It is also possible that the critical leaching flux of acid anions (AN$_{leach}$) is only exceeded by the combination of S and N leaching fluxes, i.e. S deposition < CL$_{max}$S and N deposition < CL$_{max}$N, but the sum of S and N leaching is greater than AN$_{leach}$. In this case, a reduction in either S or N deposition could prevent critical load exceedance. The FAB model may therefore be used to determine exceedance "classes" defining deposition reduction requirements in terms of compulsory or optional reductions

in S and/or N deposition to prevent critical load exceedance. For a fuller description of the use of the FAB model to determine deposition reduction requirements, see Curtis et al. (2000).

Note that there is a distinction to be made between S and N effects predicted by the FAB model. Sulphate leaching is generally assumed to be in approximate steady-state with deposition inputs so that leaching responds directly to changes in inputs and effects are "current" or "actual". Nitrate leaching, on the other hand, is regulated to a much larger degree by biological cycling and ecosystems may assimilate N for prolonged periods without a major increase in nitrate leaching. The N effects predicted by FAB should therefore be considered "potential" effects that may only be realised in the longer term (see discussion).

## Results

Some of the EMERGE lake districts are known to have calcareous geology resulting in lakes which are non-sensitive to acidification by atmospheric deposition. Water chemistry from survey lakes was therefore used to screen out lake districts where FAB model application was not required. Three lake districts (Central Alps, Julian Alps and Greenland) had survey lake populations with very high minimum ANC values (Table 1), indicating non-sensitive soils and geology and no risk of acidification. These lake districts (n = 53 lakes) were omitted from further modelling work on the basis of assumed non-exceedance of critical loads for acidity.

Piedmont Ticino had the largest proportion of survey lakes with ANC <0 µeq L$^{-1}$, while in the Retezat and Rila Mountain lake districts all lakes had ANC >20 µeq L$^{-1}$ (Fig. 1). The proportion of waters with ANC <50 µeq L$^{-1}$ varied greatly between lake districts, from around a quarter or less of survey lakes in Finland, the Pyrenees, the Rila Mountains and the Tyrol, to around two thirds in central Norway and Piedmont Ticino. The water chemistry of
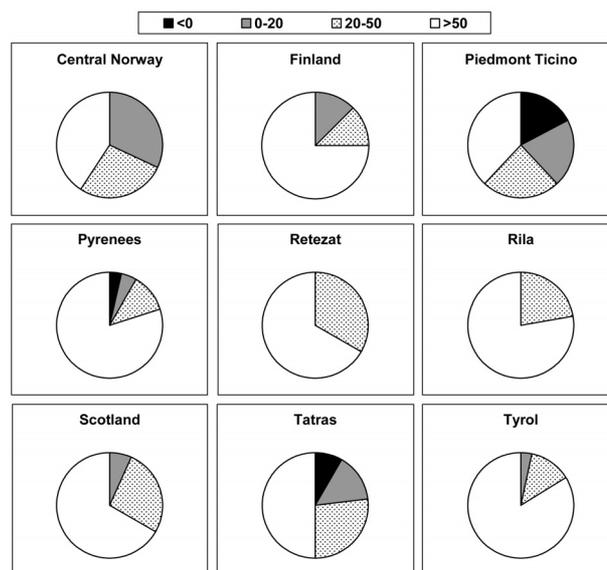


**Figure 1.** ANC distribution in survey lakes (µeq L$^{-1}$).

survey lakes is described in greater detail by Camarero et al. (submitted), but non-marine sulphate and nitrate concentration ranges are shown in Table 2. The proportion of measured sulphate that is assumed to be non-marine in origin is determined from the fixed ratio of sulphate to chloride in seawater and the assumption that measured chloride in the sample comes from marine sources only: non-marine sulphate = total measured sulphate – (0.104 × chloride).

Exceedance as a proportion of survey lake populations is presented for both values of ANC$_{crit}$ in Figure 2, showing the great variation among lake districts in both the proportion of exceeded sites and sensitivity to the choice of ANC$_{crit}$ (0 or 20 µeq L$^{-1}$). FAB model exceedance classes calculated using ANC$_{crit}$ = 0 µeq L$^{-1}$ and EMEP S and N deposition data for 2000 are shown in Table 3. Critical loads were exceeded in only four lake districts; Piedmont Ticino, the Pyrenees, the Retezat Mountains and the Tatras, the latter two regions having

**Table 3.** Numbers of lakes in FAB exceedance classes with ANC$_{crit}$ = 0 µeq L$^{-1}$.

| Lake district | Total no. of lakes | Number not exceeded | Number exceeded | % exceeded | Reduce S only | Reduce S then S or N | Reduce S and N | Reduce N then S or N | Reduce Either S or N |
|---|---|---|---|---|---|---|---|---|---|
| CN | 22 | 22 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| NF | 40 | 40 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| PT | 29 | 20 | 9 | 31 | 0 | 0 | 0 | 5 | 4 |
| PY | 85 | 76 | 9 | 12 | 0 | 0 | 1 | 3 | 5 |
| RE | 6 | 3 | 3 | 50 | 0 | 0 | 0 | 0 | 3 |
| RI | 9 | 9 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| SC | 30 | 30 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| TA | 48 | 22 | 26 | 54 | 0 | 3 | 5 | 0 | 18 |
| TY | 31 | 31 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
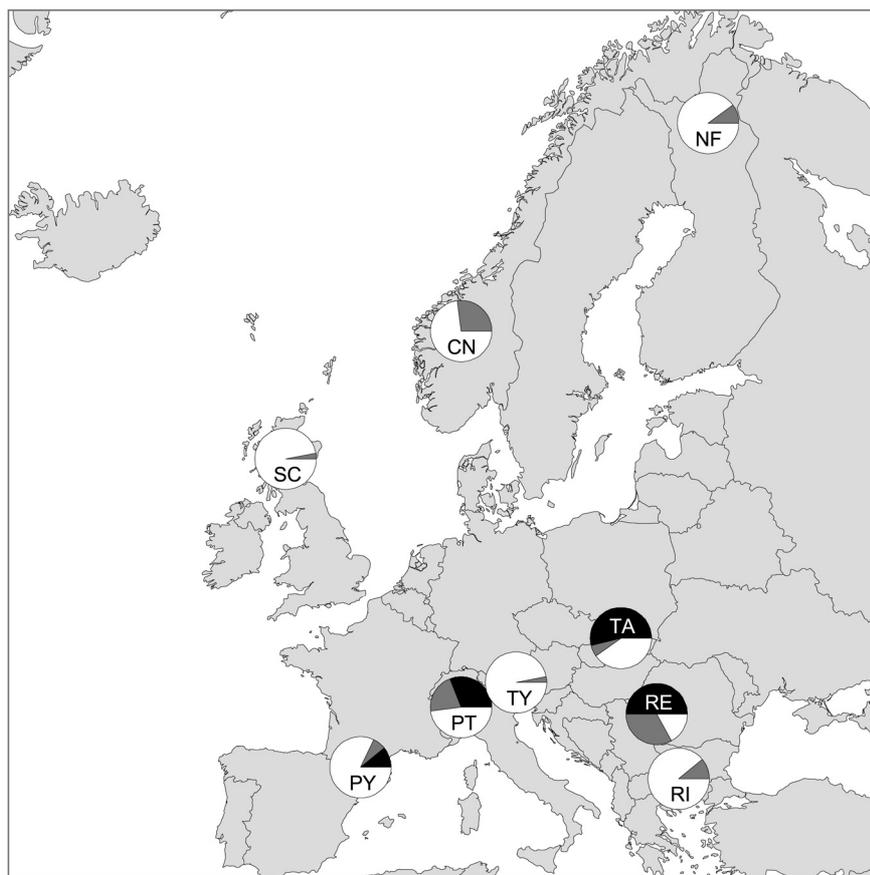
**Figure 2.** Map of percentage of survey lakes showing critical load exceedance with $ANC_{crit} = 0$ µeq $L^{-1}$ (■), additional sites showing exceedance with $ANC_{crit} = 20$ µeq $L^{-1}$ (▨) and non-exceeded sites (□). Note that sites exceeded with $ANC_{crit} = 0$ µeq $L^{-1}$ are also exceeded with $ANC_{crit} = 20$ µeq $L^{-1}$.

**Table 4.** Numbers of lakes in FAB exceedance classes with $ANC_{crit} = 20$ µeq $L^{-1}$.

| Lake district | Total no. of lakes | Number not exceeded | Number exceeded | % exceeded | Reduce S only | Reduce S then S or N | Reduce S and N | Reduce N then S or N | Reduce Either S or N |
|---|---|---|---|---|---|---|---|---|---|
| CN | 22 | 16 | 6 | 27 | 6 | 0 | 0 | 0 | 0 |
| NF | 40 | 36 | 4 | 10 | 2 | 0 | 2 | 0 | 0 |
| PT | 29 | 14 | 15 | 52 | 0 | 0 | 1 | 10 | 4 |
| PY | 85 | 70 | 15 | 18 | 0 | 0 | 4 | 5 | 6 |
| RE | 6 | 1 | 5 | 83 | 0 | 1 | 0 | 0 | 4 |
| RI | 9 | 8 | 1 | 11 | 0 | 0 | 0 | 0 | 1 |
| SC | 30 | 29 | 1 | 3 | 1 | 0 | 0 | 0 | 0 |
| TA | 48 | 19 | 29 | 60 | 0 | 4 | 14 | 0 | 11 |
| TY | 31 | 30 | 1 | 3 | 0 | 0 | 0 | 0 | 1 |

the greatest proportion of exceeded survey lakes. None of the exceeded sites fell into the FAB class "reduce S only", indicating that N contributed to exceedance at all exceeded survey lakes. In the Tatras, three of the 26 exceeded lakes were impacted mainly by S ("Reduce S then S or N"), while in Piedmont Ticino and the Pyrenees, around a half and a third of exceeded sites, respectively, were affected mainly by N ("Reduce N then S or N").

With a higher value of $ANC_{crit}$ (20 µeq $L^{-1}$) all nine lake districts considered contained lakes that exceeded their critical loads (Table 4). The relative importance of S and N in contributing to exceedance shifted in most lake districts. In two of the lake districts to show critical load exceedance only with the higher value of $ANC_{crit}$ (Central Norway and Scotland), S deposition alone was responsible, while in Northern Finland, S alone was the cause in

two of the four exceeded survey lakes. The additional site showing exceedance in the Rila Mountains could be protected by reductions in either S or N deposition.

The number of lakes requiring reductions in both S and N also increased with the higher value of $ANC_{crit}$ in Piedmont Ticino, the Pyrenees and especially the Tatras, with two of the new exceedances in Northern Finland falling into this category. These survey lakes are at risk of more severe acidification because either S or N deposition alone is sufficiently high to cause critical load exceedance.

## Discussion

Regional impacts are discussed first, followed by a more general consideration of modelling limitations and uncertainties.

### Regional impacts
*Central Norway.* In Central Norway, exceedances occurred only with $ANC_{crit} = 20$ µeq L$^{-1}$. Six of the 22 survey lakes with ANC values in the range 7–17 µeq L$^{-1}$ and pH 5.8 – 6.1 showed exceedance due solely to S deposition. The dominance of sulphate compared to nitrate in measured water chemistry data is shown in Table 2. This region of Norway experiences lower deposition and fewer exceedances than have been found in Southern Norway (Henriksen et al., 1998). EMEP scale deposition values are the lowest of all exceeded lake districts except Northern Finland, so these exceedances indicate the extreme acid-sensitivity of lakes in this region.

*Northern Finland.* With $ANC_{crit} = 20$ µeq L$^{-1}$ four of the 40 survey lakes in Northern Finland showed exceedance despite the lowest deposition values of all lake districts. The four exceeded lakes had extremely dilute waters with ANC values of 5–12 µeq L$^{-1}$ and pH in the range 5.6 – 5.8, but very low concentrations of non-marine sulphate (Table 2) meant that no sites were exceeded at $ANC_{crit} = 0$ µeq L$^{-1}$. Measured nitrate concentrations were the lowest of all lake districts (Table 2), but potential leaching predicted by FAB contributed to exceedance at two of the four sites. A similar proportion of sites with critical loads exceeded by S deposition (9%) was found in a survey of 873 lakes across the whole of Finland in 1995 (Henriksen et al., 1998).

*Piedmont Ticino.* Fifteen of the 29 survey sites were exceeded with $ANC_{crit} = 20$ µeq L$^{-1}$ and nine were still exceeded with the lower value of $ANC_{crit} = 0$ µeq L$^{-1}$. The widespread acidification in this lake district has been recorded in previous studies. For example, Boggero et al. (1998) found that in a wider survey of 55 lakes in the early 1990s, one third of lakes were extremely acid-sen-

sitive with alkalinity values <20 µeq L$^{-1}$. Potential acidification in the lake district is due more to N deposition than to S, as noted also by Camarero et al. (1995), with the current range of nitrate concentrations of 9–36 µeq L$^{-1}$ comparable to non-marine sulphate (24–45 µeq L$^{-1}$) and increased nitrate leaching predicted by FAB. Several sites were severely acidified with negative ANC values; the range for all exceeded sites was –7 to 29 µeq L$^{-1}$ and pH 5.3 – 6.5.

*Pyrenees.* Previous wide-ranging studies of Pyrenean lakes have suggested only the early signs of acidification in a small proportion of sites, with just 3.3% of lakes having alkalinity <20 µeq L$^{-1}$ (Catalan et al., 1993; Camarero et al., 1995; Camarero and Catalan, 1998). The current study indicates that a small but significant proportion of the 85 sampled Pyrenean lakes (18%) exceeded their critical loads for $ANC_{crit} = 20$ µeq L$^{-1}$, while 12% were still exceeded with $ANC_{crit} = 0$ µeq L$^{-1}$. However, Camarero and Catalan (1998) pointed out that localised catchment sources of S from oxidation of pyrites can lead to high acidity in some lakes. Inspection of the chemistry data for exceeded sites reveals that at least four of those exceeded at the higher critical ANC had sulphate concentrations one or two orders of magnitude greater than in other exceeded lakes, suggesting non-atmospheric S sources in these catchments. One of these sites with a sulphate concentration of 1239 µeq L$^{-1}$ (cf. 11–55 µeq L$^{-1}$ in most other Pyrenean lakes) was responsible for the minimum ANC value of –224 µeq L$^{-1}$ recorded for this lake district in Table 1. These lakes are geographically clustered (c. 42.6°N, 1.4°E) and their distinctive chemistry indicates localised mineralogy and spurious critical load exceedances (see below).

In the other sites showing 'genuine' exceedance of critical loads by atmospheric deposition, ANC ranged from 14 – 73 µeq L$^{-1}$ and pH from 6.1 – 7.2. The higher pH and ANC sites were marginally exceeded for $ANC_{crit} = 20$ µeq L$^{-1}$, reflecting the very high N deposition and increased nitrate leaching predicted by FAB, despite only low to moderate concentrations at present (Table 2). Nitrogen deposition was more important than S deposition in causing exceedance for most sites, and the need to incorporate N processes in critical loads models for this region was highlighted in earlier work by Camarero and Catalan (1998).

*Retezat Mountains.* The lakes in these mountains are acid sensitive despite having the highest minimum ANC value (38 µeq L$^{-1}$) of the nine regions where the FAB model was applied (Table 1). Three out of six showed exceedance with the low value of $ANC_{crit} = 0$ µeq L$^{-1}$, while the higher value resulted in five out of six being exceeded. S and N were equally important in contributing to acidification here, with the highest deposition loads for S

of all modelled lake districts. There are few published data on acidification in this region, although recent programmes have been set up to monitor the effects of air pollution on forest health and biodiversity in terrestrial ecosystems there and have found few measurable impacts (Bytnerowicz et al., 2001; 2003). The Retezat Mountain lakes are, however, clearly impacted by acid deposition, but Romania does not currently provide critical loads data to the international mapping programme that feeds into the CLRTAP.

*Rila Mountains.* Previous studies of the softwater lakes on granitic geology in the Rila Mountains found them to be slightly acidified despite little measurable change in water chemistry over several decades (Botev, 2000). Similar results have also been found in the Pirin Mountains in Bulgaria, which were shown to be highly sensitive but relatively unaffected by acid deposition (Camarero et al., 1995). The results of the current study are consistent with these findings; only one of the nine sample sites exceeded its critical load and only when $ANC_{crit}$ = 20 µeq $L^{-1}$ was used. The exceeded site (Alekevo Ezero) had a pH of 6.01 and an ANC of 31 µeq $L^{-1}$, the lowest of the sampled sites in the Rila Mountains.

*Scotland.* Like the Rila Mountains, the Scottish lake district had only one site (57.517°N, –5.392°E, sitecode SC0084) showing exceedance and only for $ANC_{crit}$ = 20 µeq $L^{-1}$. The site had a pH of 5.45 and the lowest ANC value for the sampled sites of only 16 µeq $L^{-1}$, showing extreme acid sensitivity. However, this site was the only one of all the exceeded sites for which the calculated non-marine concentration of sodium (calculated from the constant composition of seawater as Na – (0.86 × Cl) with concentrations in equivalents) was negative. Sea-salt driven acidification, whereby high concentrations of marine base cations displace acidic cations ($H^+$, $Al^{3+}$) from the soil exchange matrix (Harriman et al., 1995) may therefore be a factor at this site, as suggested also by the extremely low non-marine sulphate concentration (Table 2).

Wider ranging studies of critical load exceedance in Scotland have produced varied results. A random survey of Scottish lochs representing 1.6% of the total loch population found that only 1% of those sampled were exceeded by S deposition alone (Henriksen et al., 1998). However, Curtis et al. (2000) found a much larger proportion of exceeded sites (both lochs and streams) sampled on the basis of acid-sensitive soils and geology, with 22% of 754 sites showing exceedance and S deposition as the major agent of acidification. Surface water acidification in Scotland is well known in southern areas outside the EMERGE mountain loch district and closer to emissions sources (Galloway – Wright et al., 1994; Ferrier et al., 1995) but has also been detected in mountain lochs in

the Cairngorm region (Helliwell et al., 2002) where some of the current survey sites are located. The low percentage of exceeded sites in the current study and the small subsample of mountain lochs surveyed (7.5%) could therefore mean that acidified mountain lochs in Scotland are under-represented by survey sites within this lake district.

*Tatra Mountains.* Severe acidification in the Tatra Mountains of Poland and Slovakia, with an increase in strong acid anion concentrations of up to 109 µeq $L^{-1}$ between the 1930s and 2000, is well recorded in the literature (Fott et al., 1994; Kopáček and Stuchlík, 1994; Kopáček et al., 2001) while evidence of more recent chemical and biological recovery has also been reported (Kopáček et al., 1998). Results from the current modelling exercise are broadly consistent with previous studies. 26 of the 48 survey lakes (54%) showed exceedance with $ANC_{crit}$ = 0 µeq $L^{-1}$ and 29 (60%) were exceeded with $ANC_{crit}$ = 20 µeq $L^{-1}$, compared with the classification of 21 out of 53 sampled lakes (40%) as acidified by Kopáček and Stuchlík (1994). The relative similarity in exceedance figures between the two values of $ANC_{crit}$ reflects the severity of acidification in these sites, making them insensitive to the choice of $ANC_{crit}$. Measured ANC in exceeded sites ranged from –32 to 87 µeq $L^{-1}$ while the pH range was 4.8 to 6.7. Total acid deposition (S+N) is greater in this lake district than elsewhere, with S being more important than N in causing exceedance despite the large reductions in emissions over the last 20 years and the results of a previous study in the Polish Tatras suggesting that N deposition was critical in causing exceedance (Henriksen et al., 1992b). The mean nitrate concentration in exceeded sites is the highest of all lake districts (Table 2) and the continued dominant role of S in causing exceedance is due to the very high S deposition levels still found in this region.

*Tyrol.* Of the 31 survey sites in the Tyrol, only one site (Mutterbergersee) showed critical load exceedance, and only at the higher value of $ANC_{crit}$ = 20 µeq $L^{-1}$. Deposition is moderately low at this site, but the pH of 5.7 and ANC of 8 µeq $L^{-1}$ reflect its great acid-sensitivity. Previous studies in the Tyrol have found that while a large proportion of mountain lakes are acidic, weathering sources of sulphate are often responsible rather than deposition sources (Camarero et al., 1995). Palaeolimnological studies have also linked changes in lake water acidity to climate as well as acid deposition (Psenner and Schmidt, 1992; Sommaruga-Wögrath et al., 1997). Hence the extent of acidification due primarily to acid deposition is difficult to ascertain. A low sulphate concentration in the exceeded site compared with other sites elsewhere does, however, suggest that weathering sources of S are not the cause of acidification here.

## Input and output fluxes of acid anions

The basis of the FAB model is a mass balance for the major acid anions sulphate and nitrate, with the assumption that leached inorganic N will be in the form of nitrate even if originating from the deposition of reduced N. The leaching fluxes of sulphate and nitrate predicted by FAB are thus equal to the difference between deposition flux

### a. Non-marine sulphur



### b. Total inorganic N
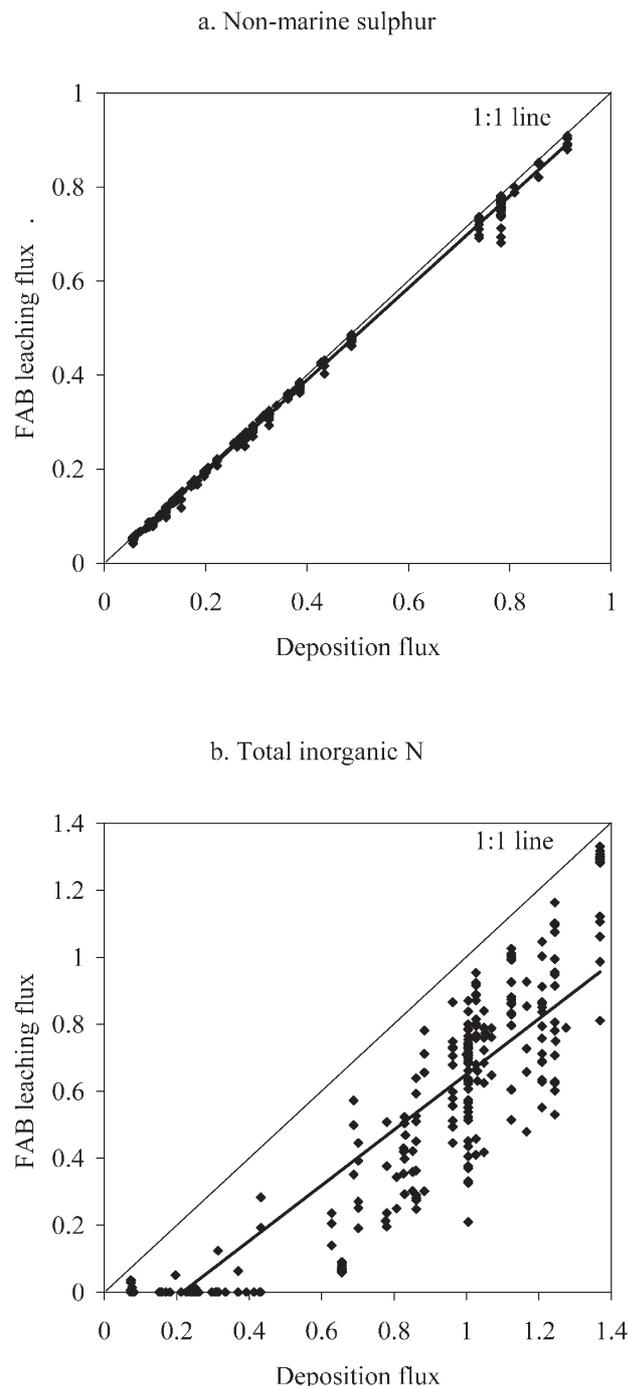


**Figure 3.** FAB modelled leaching flux vs. EMEP modelled deposition flux of acid anions (keq ha$^{-1}$ yr$^{-1}$).

and retention in soil and lake used in the model. For non-marine sulphur (Fig. 3a) only a very small proportion of S (c. 2%) is assumed to be retained in lakes by biological uptake or reduction in sediments, so that input and output fluxes are almost equal (FAB leaching = 0.98 deposition – 0.002, $R^2$ = 0.998, P < 0.0001). A much greater proportion of total inorganic N (TIN) deposition is retained in both catchment soils and the lake itself according to the model (see trendline in Fig. 3b: FAB leaching = 0.83 deposition – 0.18; $R^2$ = 0.826, P < 0.0001). The variation in predicted leaching flux of TIN for a given value of deposition (vertical spread in Fig. 3b) reflects the variation in peat cover, proportional soil cover of catchments and lake:catchment area ratio.

Current leaching fluxes of acid anions can be estimated from measured concentrations (assumed to be representative of annual volume-weighted mean) and runoff (assumed to be 80% of precipitation). Although major assumptions were made in the calculation of leaching fluxes for S, there is much greater scatter in the data than might be expected (Fig. 4a), in particular the very high leaching fluxes of S that greatly exceed deposition inputs. There is no correlation between estimated input and output fluxes. This may be due to two factors. First, it is known that in some regions (e.g. Pyrenees, Tyrol, Malé Hincovo in the Tatras) there are geological sources of S which could result in greater leaching fluxes than are predicted from deposition alone. The second source of uncertainty lies in the deposition data, which are modelled at a very coarse resolution.

Comparison of the range of non-marine sulphate concentrations in all sites and in exceeded sites only shows that in all lake districts except the Pyrenees, the mean non-marine sulphate concentration is lower in exceeded sites than in the sample population (Table 2). These data suggest that in most lake districts, large weathering inputs of sulphate are associated with large inputs of base cations and alkalinity, possibly due to calcareous geology, resulting in high ANC values and non-exceedance of critical loads. In the Pyrenees, the mean non-marine sulphate concentration is much higher in the exceeded population of sites than in the whole sample population, suggesting that weathering sources of sulphate are instead linked with oxidation of pyrites and not with large weathering inputs of alkalinity, leading to more acid water chemistry. Figure 4b shows that in the exceeded lakes, most of the sites with extremely high leaching fluxes of S relative to deposition inputs are absent. Overall, it is therefore concluded that the only lake district where weathering sources of S may contribute significantly to the generation of spurious critical load exceedances is the Pyrenees.

Camarero et al. (submitted), using a factor analysis of lake chemistry and environmental variables, concluded that a lake-water concentration of 50 µeq L$^{-1}$ best separated those sites where sulphate was correlated with S de-
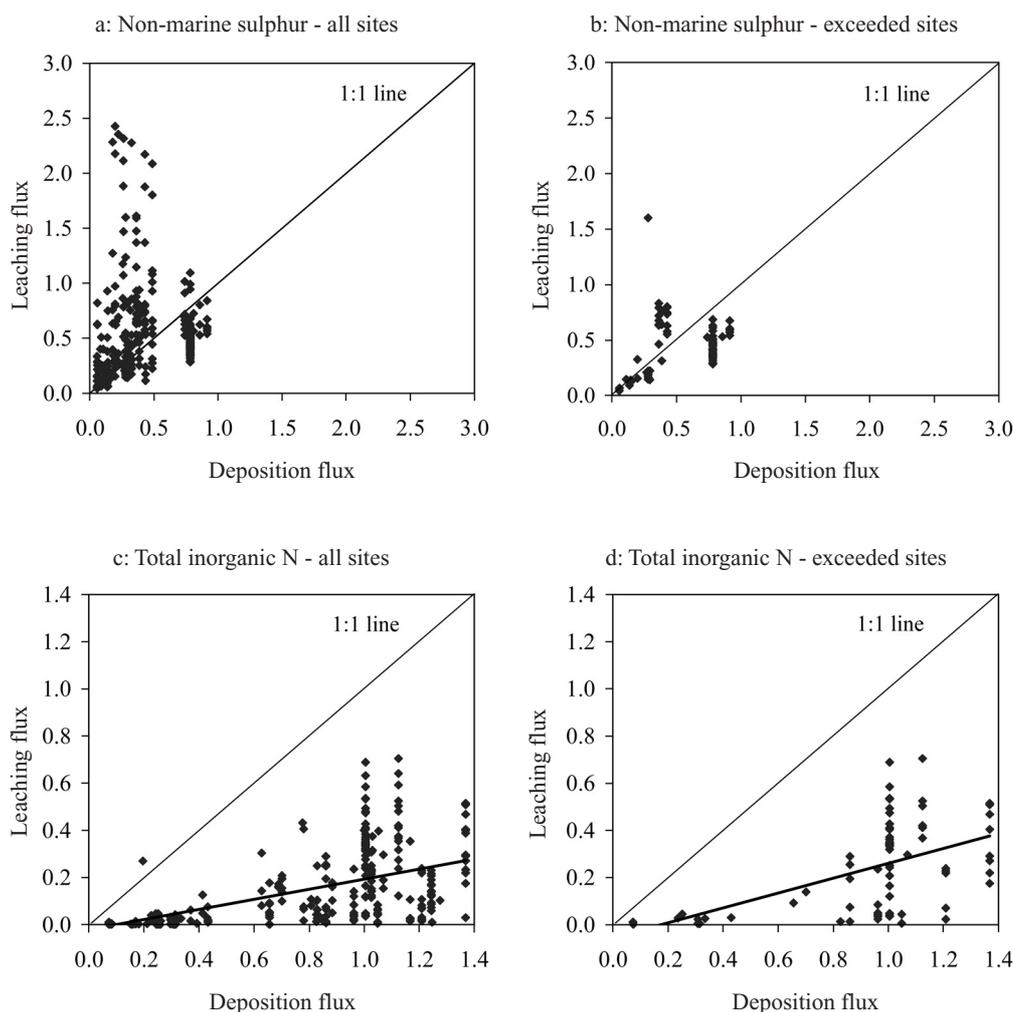
**Figure 4.** Estimated (measured) leaching flux vs. modelled EMEP deposition flux of acid anions (keq ha$^{-1}$ yr$^{-1}$) for all survey lakes (n = 300) and sites exceeding critical load for ANC$_{crit}$ = 20 μeq L$^{-1}$ (n = 77).

position (<50 μeq L$^{-1}$) and those with major weathering sources of sulphate (>50 μeq L$^{-1}$). If sites with sulphate concentrations >50 μeq L$^{-1}$ are removed from the exceedance statistics, the only lake districts affected are the Pyrenees and the Retezat Mountains. With ANC$_{crit}$ = 0 μeq L$^{-1}$ the number of exceeded sites in the Pyrenees is reduced from nine to six (from 11 to 7%) and in the Retezat Mountains from three to one (50% to 17%). With ANC$_{crit}$ = 20 μeq L$^{-1}$ the number of exceeded sites in the Pyrenees declines from 15 to nine (from 18 to 11%) and in the Retezat Mountains from five to two (83% to 33%). Hence the presence of weathering sources of S in parts of the Pyrenees is further supported by this exercise. In the Retezat Mountains the picture is less clear if the data in Table 2 are considered, because this region receives the highest modelled S deposition which, when converted into a concentration in runoff using mean values, would result in a sulphate concentration of 70 μeq L$^{-1}$, compared with 25 μeq L$^{-1}$ in the Pyrenees. For the Retezat Moun-

tain lakes, the measured sulphate concentrations therefore fall within the range that could be due entirely to atmospheric deposition inputs, whereas concentrations in many of the Pyrenean lakes could not be due solely to deposition inputs (Table 2).

TIN leaching flux is weakly but highly significantly correlated with TIN deposition flux in all survey sites (see trendline in Fig. 4c: leaching = 0.21 deposition - 0.02, R$^2$=0.309, P<0.0001), with a similar spread of data in exceeded sites (Fig. 4d). Comparison of the trendlines in Figs. 3b and 4c shows the degree of increased nitrate leaching assumed by the FAB model relative to current estimated leaching fluxes from measured data. It is a well-known feature of the FAB model that predicted nitrate leaching fluxes are generally much greater than observed fluxes because of the very small long-term sinks assumed to exist in these upland systems, and it should be recognised that the predicted leaching fluxes may not be achieved for many decades as short-term N sinks accu-

mulate deposited N (Curtis et al., 1998). Furthermore, there are large uncertainties associated with the long-term sinks for N in upland catchments which are the focus of major ongoing research programmes in, for example, the U.K. (Curtis and Simpson, 2001) and Norway (Henriksen and Hessen, 1997).

**Uncertainties in modelling approach**

A major source of uncertainty in critical load exceedance calculations results from the use of EMEP scale deposition data on a 50 km grid, as altitude is an important factor in determining local deposition load. At higher altitudes, the seeder-feeder effect may increase total deposition load, so that values averaged over a large area may overestimate deposition to lower altitude sites and underestimate deposition to higher altitude sites. However, distance to sources of acid emissions is also an important factor. Hence in complex mountainous terrain, local variations in deposition load within a $50 \times 50$ km square will be very large, with significant underestimates possible for the highest altitude sites (Hirst and Storvik, 2003). This variation cannot be easily quantified in such remote areas where deposition monitoring stations are sparsely located.

Parameterisation of the FAB model is also a source of uncertainties, since assumptions have to be made where data are unavailable. For example, it was assumed in the modelling exercise that in alpine soils, sustainable immobilisation rates for N ($N_{imm}$) in catchment soils are likely to be very low and at the bottom end of ranges described in the literature, because of the generally thin and poorly-developed nature of alpine soils. For this reason, a low value of $N_{imm} = 0.5$ kgN ha$^{-1}$ yr$^{-1}$ was used (UBA, 1996; Hall et al., 1997). However, long-term immobilisation processes and their responses to elevated N deposition are poorly understood, with most existing data based on chronosequence studies of soil age and total N storage. If increased N supply from anthropogenic deposition were to increase the formation of recalcitrant organic N compounds in soils, then current long-term immobilisation rates could exceed those found in the past.

A re-run of the FAB model with $ANC_{crit} = 20$ µeq L$^{-1}$ and $N_{imm}$ set to a mid-range value from the literature of 1.5 kgN ha$^{-1}$ yr$^{-1}$ instead of 0.5 kgN ha$^{-1}$ yr$^{-1}$ results in a reduction in the number of exceeded sites in six of the nine lake districts, with the single sites exceeded previously in the Rila Mountains and the Tyrol no longer showing exceedance. No change in numbers exceeded are found in Central Norway, Northern Finland and Scotland, although the absolute magnitude of exceedance at individual sites may be reduced as less N is available for leaching in the long-term. The proportion of sites exceeded in the remaining lake districts is reduced as follows; Piedmont Ticino from 52 to 45%, Pyrenees from 18 to 11%, Retezat Mountains from 83 to 33% and the Tatras from 65 to 54%. The effects are, not surprisingly, most pronounced in those lake districts where calculated exceedances were most marginal, and illustrate the importance of further research into nitrogen retention processes and leaching mechanisms in these mountain lake catchments. Overall, however, the effect of using the high value of $N_{imm}$ is relatively minor, showing that uncertainty in this term does not significantly affect the conclusions of this study.

Another source of uncertainty in the model relates to the literature-based mass-transfer coefficients used to calculate in-lake retention of S and N, given the lack of input-output budgets for mountain lakes on which to base site-specific or even regional estimates. However, the mid-range values used ($S_N = 5$ m yr$^{-1}$ and $S_S = 0.5$ m yr$^{-1}$) were found to be appropriate for acid-sensitive lakes in southern Norway as well as the original North American lakes on which the literature values were originally based (Kaste and Dillon, 2003). Furthermore, re-runs of the FAB model show that calculated exceedances are not very sensitive to changes in the mass-transfer coefficients used. With the lower-end values of $S_N = 2$ m yr$^{-1}$ and $S_S = 0.2$ m yr$^{-1}$ the only changes to the number of exceeded sites occurred in the Pyrenees (increase from 18% to 24%) and the Retezat Mountains, where the one previously non-exceeded site with $ANC_{crit} = 20$ µeq L$^{-1}$ is now exceeded. Using the uppermost mass-transfer coefficient values of $S_N = 8$ m yr$^{-1}$ and $S_S = 0.8$ m yr$^{-1}$ only the exceeded populations of the Pyrenees (reduced from 18 to 15%) and the Tatras (reduced from 65 to 58%) are changed. Hence the use of the mid-range values for in-lake mass-transfer coefficients in this exercise does not greatly affect the regional distributions of critical load exceedance.

**Conclusions**

European mountain lakes are not universally sensitive to acid deposition. In mountain regions of calcareous geology (e.g. Central Alps and the Julian Alps of Slovenia) lake acidification will never be a problem, although chemistry and biology may be affected by other pollutants or climatic changes. Even in areas of crystalline geology, the remoteness of mountain lakes from the anthropogenic sources of acid emissions protects many of them from the adverse effects of acid deposition. However, depending on the choice of $ANC_{crit}$ used in the FAB model, all nine modelled lake districts show critical load exceedance to varying extents, indicating the presence of at least some highly sensitive mountain lakes. In two lake districts, the Retezat Mountains of Romania and the Rila Mountains of Bulgaria, critical load exceedance is reported here for the first time.

With the lower value of ANC$_{crit}$ = 0 μeq L$^{-1}$, four lake districts showed critical load exceedance (Piedmont Ticino, the Pyrenees, the Retezat Mountains and the Tatras) indicating that modelled atmospheric deposition is sufficiently high to depress ANC below zero at steady-state (i.e. with enhanced nitrate leaching) in some of the mountain lakes in these areas. These lake districts are therefore potentially the most severely acidified.

At the higher value of ANC$_{crit}$ = 20 μeq L$^{-1}$, all lake districts showed critical load exceedance in at least one sampled site. The four lake districts showing the lowest proportions of exceeded sites were Northern Finland, the Rila Mountains, Scotland and the Tyrol. The greatest proportion of exceeded sites was generally found in those lake districts showing exceedance at the lower value of ANC$_{crit}$.

While the survey sites modelled here were found to be representative of the population of mountain lakes in each lake district on the basis of remotely sensed physical catchment attributes (Curtis et al., 2005), there are two major factors introducing uncertainty into the critical load exceedance values. Spurious (over-estimated) exceedances may be locally significant in regions of sulphur bearing geology in the Pyrenees, where it may be difficult to separate the relative contributions of climate change driven effects on sulphate release from pyrite oxidation and acid deposition in causing changes in acidity status of lakes. Secondly, the low resolution EMEP deposition data used could grossly underestimate the actual total acid deposition loads experienced by mountain lakes, so that the extent and degree of critical load exceedance are both under-represented here.

## Acknowledgments

## References

Boggero, A., A. Barbieri, J. de Jong, A. Marchetto and R. Mosello, 1998. Chemistry and critical loads of Alpine lakes in Canton Ticino (Southern Central Alps). Aquat. Sci. **60:** 300–315.

Botev, I. S., 2000. Chemical composition and its vertical distribution in seven glacial high altitude lakes in the Rila Mountains (southwestern Bulgaria). In: V. Golemansky and W. Naidenow (eds.), Biodiversity and Evolution of Glacial Water Ecosystems in the Rila Mountains, Institute of Zoology, Bulgarian Academy of Sciences, Sofia, pp. 89–104.

Brakke, D. F., A. Henriksen and S. A. Norton, 1990. A variable F-factor to explain changes in base cation concentrations as a function of strong acid deposition. Verh. Internat. Verein. Limnol. **24:** 146–149.

Bull, K. R., 1991. The critical loads/levels approach to gaseous pollutant emission control. Environ. Pollut. **69:** 105–123.

Bytnerowicz, A., O. Badea, F. Popescu, I. Barbu, D. PstelNicu, C. Vasile, R. Musselman, W. Manning, E. Stanciu and S. Tamas, 2001. Long-term ecological research and air pollution impacts in the Retezat Mountains, Romania. Ekologia-Bratislava **20:** 34–42.

Bytnerowicz, A., O. Badea, I. Barbu, P. Fleischer, W. Fraczek, V. Gancz, B. Godzik, K. Grodzinska, W. Grodzki, D. Karnosky, M. Koren, M. Krywult, Z. Krzan, R. Longauer, B. Mankovska, W. J. Manning, M. McManus, R. C. Musselman, J. Novotny, F. Popescu, D. PstelNicu, W. Prus-Glowacki, P. Skawinski, S. Skiba, R. Szaro, S. Tamas and C. Vasile, 2003. New international long-term ecological research on air pollution effects on the Carpathian Mountain forests, Central Europe. Environment International **29:** 367–376.

Camarero, L., J. Catalan, R. Psenner, A. Boggero, A. Marchetto and R. Mosello, 1995. Acidification in high mountain lakes in central, southwest and southeast Europe (Alps, Pyrenees, Pirin). Limnologica **25:** 141–56.

Camarero, L. and J. Catalan, 1998. A simple model of regional acidification for high mountain lakes: application to the Pyrenean lakes (north-east Spain). Wat. Res. **32:** 1126–36.

Camarero, L., M. Rogora, R. Mosello, N. J. Anderson, A. Barbieri, I. Botev, A. Brancelj, C. Postolache, M. Kernan, A. Korhola, A. Lotter, E. Stuchlík, H. Thies and R. F. Wright (submitted). Regionalisation of chemical variability in European mountain lakes.

Casals-Carrasco, P., M. Ventura, J. L. Pretus, V. Gond, B. Madhavan and J. Catalan (submitted). A spectral approach to land-cover classification in remote mountain lake areas.

Catalan, J., E. Ballesteros, E. Gacia, A. Palau and L. Camarero, 1993. Chemical composition of disturbed and undisturbed high mountain lakes in the Pyrenees: a reference for acidified sites. Wat. Res. **27:** 133–141.

Curtis, C. J., T. E. H. Allott, B. Reynolds and R. Harriman, 1998. The prediction of nitrate leaching with the first-order acidity balance (FAB) model for upland catchments in Great Britain. Water, Air and Soil Pollut. **105:** 205–215.

Curtis, C. J., T. E. H. Allott, M. Hughes, J. Hall, R. Harriman, R. Helliwell, M. Kernan, B. Reynolds and J. Ullyett, 2000. Critical loads of sulphur and nitrogen for freshwaters in Great Britain and assessment of deposition reduction requirements with the First-order Acidity Balance (FAB) model. Hydrology and Earth System Sciences **4:** 125–140.

Curtis, C. J., A. Barbieri, L. Camarero, M. Gabathuler, J. Galas, K. Hanselmann, J. Kopáček, R. Mosello, N. Rose, E. Stuchlik, H. Thies, U. Nickus, M. Ventura and R. Wright, 2002. Application of static critical load models for acidity to high mountain lakes in Europe. Water, Air and Soil Pollution: Focus **2:** 115–126.

Curtis, C. J., M. Posch, P. Casals-Carrasco, J. Catalan, M. Hughes, M. Kernan and M. Ventura, 2005. The significance of European high mountain lakes in critical load distributions at the EMEP grid scale. Aquat. Sci. **67:** in press.

Curtis, C. and G. Simpson (eds.), 2001. Summary of Research under DETR Contract "Acidification of freshwaters: the role of nitrogen and the prospects for recovery", EPG1/3/117. ECRC Research Report No.79, Environmental Change Research Centre, University College London, UK, 4 Volumes.

Dillon, P. J. and L. A. Molot, 1990. The role of ammonium and nitrate retention in the acidification of lakes and forested catchments. Biogeochemistry **11:** 23–43.

Evans, C. D., J. M. Cullen, C. Alewell, J. Kopáček, A. Marchetto, F. Moldan, A. Prechtel, M. Rogora, J. Vesely and R. Wright, 2001. Recovery from acidification in European surface waters. Hydrology and Earth System Sciences **5:** 283–297.

EU, 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for

Community action in the field of water policy. Official Journal L **327**: 1–73.

Ferrier, R. C., A. Jenkins, B. J. Cosby, R. C. Helliwell, R. F. Wright. and A. J. Bulger, 1995. Effects of future N deposition scenarios on the Galloway region of SW Scotland using a coupled sulphur & nitrogen model (MAGIC-WAND). Water, Air and Soil Pollution **85**: 707–712.

Forsius, M., S. Kleemola, J. Vuorenmaa and S. Syri, 2001. Fluxes and trends of nitrogen and sulphur compounds at integrated monitoring sites in Europe. Water, Air and Soil Pollution **130**: 1641–1648.

Fott, J., M. Pražáková, E. Stuchlík and Z. Stuchlíková, 1994. Acidification of lakes in Šumava (Bohemia) and in the High Tatra Mountains (Slovakia). Hydrobiologia **274**: 37–47.

Grimalt, J. O., P. Fernandez, P. Berdié, R. M. Vilanova, J. Catalan, R. Psenner, R. Hofer, P. G. Appleby, B. -O. Rosseland, L. Lien, J. C. Massabuau and R. W. Battarbee, 2001. Selective trapping of organochlorine compounds in mountain lakes of temperate areas. Env. Sci. Tech. **35**: 2690–2697.

Hall, J., M. Hornung, P. Freer-Smith, P. Loveland, I. Bradley, S. Langan, H. Dyke, J. Gascoigne and K. Bull, 1997. Current Status of UK Critical Loads Data - December 1996. ITE Monks Wood, UK, 22pp plus appendices.

Harriman, R., H. Anderson and J. D. Miller, 1995. The role of seasalts in enhancing and mitigating surface water acidity. Water, Air and Soil Pollution **85**: 553–558.

Helliwell, R. C. and M. Kernan, 2004. Modelling hydrochemical and ecological trends in acid sensitive surface waters in the Scottish Highlands. J. Limnol. **63**: 111–122.

Helliwell, R., R. F. Wright, C. D. Evans, A. Jenkins and R. C. Ferrier, 2002. A comparison of loch chemistry from 1955 and 1999 in the Cairngorms, N.E. Scotland. Water, Air and Soil Pollution: Focus **2**: 47–59.

Henriksen, A., 1984. Changes in base cation concentration due to freshwater acidification. Verh. Internat. Verein. Limnol. **22**: 692–698.

Henriksen, A., 1998. Application of the First-order Acidity Balance (FAB) Model to Norwegian Surface Waters. Report SNO 3809-98, Norwegian Institute for Water Research (NIVA), Oslo, Norway, 33 pp.

Henriksen, A. and D. O. Hessen, 1997. Whole catchment studies on nitrogen cycling: nitrogen from mountains to fjords. Ambio **26**: 254–257.

Henriksen, A. and M. Posch, 2001. Steady-state models for calculating critical loads of acidity for surface waters. Water, Air and Soil Pollution: Focus **1**: 375–398.

Henriksen, A., J. Kämäri, M. Posch and A. Wilander, 1992a. Critical loads of acidity: Nordic surface waters. Ambio **21**: 356–363.

Henriksen, A., W. A. Mill, M. Kot, D. Rzychon and B. Wathne, 1992b. Critical Loads of Acidity to Surface Waters: a Case Study from the Polish Tatra Mountains. Acid Rain Research Report 29/1992, NIVA, Oslo, Norway, 34pp.

Henriksen, A., B. L. Skjelkvåle, J. Mannio, A. Wilander, R. Harriman, C. Curtis, J. P. Jensen, E. Fjeld and T. Moiseenko, 1998. Northern European Lake Survey - 1995: Finland, Norway, Sweden, Denmark, Russian Kola, Russian Karelia, Scotland and Wales. Ambio **27**: 80–91.

Hirst, D. and G. Storvik, 2003. Estimating critical load exceedance by combining the EMEP model with data from measurement stations. Sci. Tot. Env. **310**: 163–170.

Kaste, Ø. and P. J. Dillon, 2003. Inorganic nitrogen retention in acid-sensitive lakes in southern Norway and southern Ontario, Canada – a comparison of mass balance data with an empirical N retention model. Hydrological Processes **17**: 2393–2407.

Kelly, C. A., J. W. M. Rudd., R. H. Hesslein, D. W. Schindler, P. J. Dillon, C. T. Driscoll, S. A. Gherini and R. E. Hecky, 1987. Prediction of biological acid neutralization in acid sensitive lakes. Biogeochemistry **3**: 129–140.

Kopáček, J. and E. Stuchlík, 1994. Chemical characteristic of lakes in the High Tatra Mountains, Slovakia. Hydrobiologia **274**: 49–56.

Kopáček, J., J. Hejzlar, E. Stuchlík, J. Fott and J. Vesely, 1998. Reversibility of acidification of mountain lakes after reduction in nitrogen and sulphur emissions in Central Europe. Limnol. Oceanogr. **43**: 357–361.

Kopáček, J., J. Vesely and E. Stuchlík, 2001. Sulphur and nitrogen fluxes and budgets in the Bohemian Forest and Tatra Mountains during the Industrial Revolution (1850–2000). Hydrology and Earth System Sciences **5**: 391–405.

Lien, L., G. G. Raddum, A. Fjellheim and A. Henriksen, 1996. A critical limit for acid neutralizing capacity in Norwegian surface waters, based on new analyses of fish and invertebrate responses. Sci. Tot. Env. **177**: 173–93.

Marchetto, A., R. Mosello, R. Psenner, A. Barbieri, G. Bendetta, D. Tait and G. A. Tartari, 1994. Evaluation of the level of acidification and the critical loads for Alpine lakes. Ambio **23**: 150–154.

MOLAR Water Chemistry Group, 1999. The MOLAR Project: atmospheric deposition and lake water chemistry. J. Limnol. **58**: 88–106.

Mosello, R. and B. M. Wathne, 1997. Surface water. Chemical analysis of major ions and nutrients. Analytical quality control. In: Wathne, B.M (Ed.). MOLAR. Measuring and Modelling the Dynamic Response of Remote Mountain Lake Ecosystem to Environmental Change: A Programme of Mountain Lake Research. MOLAR Project Manual. NIVA Report 0-96061: 24–45.

Mosello, R., B. M. Wathne and S. Van den Berg, 1997. Surface water. Sampling and analysis protocol. In: Wathne, B.M (editor). MOLAR. Measuring and Modelling the Dynamic Response of Remote Mountain Lake Ecosystem to Environmental Change: A Programme of Mountain Lake Research. MOLAR Project Manual. NIVA Report 0-96061: 20–23.

Mosello, R., A. Lami, A. Marchetto, M. Rogora, B. Wathne, L. Lien, J. Catalan, L. Camarero, M. Ventura, R. Psenner, K. Koinig, H. Thies, S. Sommaruga-Wögrath, U. Nickus, D. Tait, B. Thaler, A. Barbieri and R. Harriman, 2002. Trends in the water chemistry of high altitude lakes in Europe. Water, Air and Soil Pollution: Focus **2**: 75–89.

Posch, M., J. Kämäri, M. Forsius, A. Henriksen and A. Wilander, 1997. Exceedance of critical loads for lakes in Finland, Norway, and Sweden: reduction requirements for acidifying nitrogen and sulphur deposition. Environmental Management **21**: 291–304.

Psenner, R. and R. Schmidt, 1992. Climate-driven pH control of remote alpine lakes and effects of acid deposition. Nature **356**: 781–783.

Rogora, M., A. Marchetto and R. Mosello, 2001. Trends in the chemistry of atmospheric deposition and surface waters in the Lago Maggiore watershed. Hydrol. Earth System Sci. **5**: 379–390.

Simpson, D., H. Fagerli, J. E. Jonson, S. Tsyro, P. Wind and J. Tuovinen, 2003. EMEP Status Report 1/2003: "Transboundary Acidification, Eutrophication and Ground Level Ozone in Europe, Part I. Unified EMEP Model Description." EMEP/MSC-W Report: 104 pp.

Skjelkvåle, B. L. and R. F. Wright, 1998. Mountain lakes: sensitivity to acid deposition and global climate change. Ambio **27**: 280–286.

Sommaruga-Wögrath, S., K. A. Koinig, R. Schmidt, R. Sommaruga, R. Tessadri and R. Psenner, 1997. Temperature effects on the acidity of remote alpine lakes. Nature **387**: 64–67.

Stoddard, J. L., D. S. Jeffries, A. Lükewille, T. A. Clair, P. J. Dillon, C. T. Driscoll, M. Forsius, M. Johannessen, J. S. Kahl, J. H. Kellogg, A. Kemp, J. Mannio, D. T. Monteith, P. S. Murdoch, S. Patrick, A. Rebsdorf, B. L. Skjelkvåle, M. P. Stainton, T. Traaen, H. van Dam, K. E. Webster, J. Wieting and A. Wilander,

1999. Regional trends in aquatic recovery from acidification in North America and Europe. Nature **401:** 575–578.

UBA, 1996. Manual on Methodologies and Criteria for Mapping Critical Levels/loads and Geographical Areas Where They Are Exceeded. Report for the UN ECE Convention on Long Range Transboundary Air Pollution. Texte 71/96, Federal Environment Agency (Umweltbundesamt), Berlin, Germany, 142 pp plus Appendices.

Wright, R. F., B. J. Cosby, R. C. Ferrier, A. Jenkins, A. J. Bulger and R. Harriman, 1994. Changes in the acidification of lochs in Galloway, southwestern Scotland, 1979–1988: the MAGIC model used to evaluate the role of afforestation, calculate critical loads and predict fish status. J. Hydrol. **161:** 257–285.

To access this journal online:
http://www.birkhauser.ch