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# Relationship between critical load exceedances and empirical impact indicators at Integrated Monitoring sites across Europe

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## Abstract

Critical loads for acidification and eutrophication and their exceedances were determined for a selection of ecosystem effects monitoring sites in the Integrated Monitoring programme (UNECE ICP IM). The level of protection of these sites with respect to acidifying and eutrophying deposition was estimated for 2000 and 2020. In 2020 more sites were protected from acidification (67 %) than in 2000 (61%). However, due to the sensitivity of the sites, even the maximum technically feasible emission reductions scenario would not protect all sites from acidification. In 2000, around 20% of the IM sites were protected from eutrophication. In 2020, under reductions in accordance with current legislation, about one third of the sites would be protected, and at best, with the maximum technically feasible reductions, half of the sites would be protected from eutrophication. Data from intensively monitored sites, such as those in ICP IM, provide a connection between modelled critical thresholds and empirical observations, and thus an indication of the applicability of critical load estimates for natural ecosystems. Across the sites, there was good correlation between the exceedance of critical loads for acidification and key acidification parameters in runoff water, both with annual mean fluxes and concentrations. There was also evidence of a link between exceedances of critical loads of nutrient nitrogen and nitrogen leaching. The collected empirical data of the ICP IM thus allow testing and validation of key concepts used in the critical load calculations. This increases confidence in the European-scale critical loads mapping used in integrated assessment modelling to support emission reduction agreements.

## 1. Introduction

Critical loads are deposition thresholds used to describe the sensitivity of ecosystems to air-borne pollution. A critical load is defined as ”a quantitative estimate of an 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 and Grennfelt, 1988). The

lower the critical load, the more sensitive the ecosystem is considered to be. The critical loads and levels approach for pollution control has gathered momentum over the past two decades, and has been successfully used in strategies for emission reductions under the United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution (LRTAP) and the EU National Emission Ceilings Directive (Hettelingh et al., 2007; Amann et al., 2011).

The integrated assessment of emissions and effects of air pollutants relies on critical loads for acidification and eutrophication to quantify risks of ecosystem damage. In 2000, 12% of the ecosystem area in Europe was at risk of acidification and 54% at risk of eutrophication, according to an analysis based on critical loads (Hettelingh et al., 2011). Critical loads have also been used to assess impacts of air pollutants in North America (Ouimet et al., 2006; Pardo et al., 2011) and in the Arctic and Sub-Arctic (Forsius et al., 2010).

Empirical scientific evidence based on environmental monitoring programmes is essential for documenting the ecosystem benefits of costly emission reduction policies. The multidisciplinary International Cooperative Programme of Integrated Monitoring (UNECE ICP IM) under the LRTAP Convention quantifies pollutant effects on the environment through monitoring, modelling and scientific review, using data from catchments/plots located in predominantly forested natural or semi-natural areas (ICP IM Manual, 1998; Forsius et al., 2001; Forsius et al., 2005). Results of ICP IM provide a valuable means to study the link between critical thresholds of acidification and eutrophication of ecosystems and empirical impact indicators.

This paper has two aims: i) to calculate site-specific critical loads and their exceedances for acidification and eutrophication for terrestrial and aquatic ecosystems at selected European ICP IM sites using mass balance methods and empirical values of critical loads of nutrient nitrogen, and modelled historical and future sulphur (S) and nitrogen (N) depositions; and ii) to present relationships between the exceedances of critical loads and empirical impact indicators evaluated on the basis of surface water chemistry measurements at IM sites.

## 2. Materials and methods

### 2.1 Critical loads for acidification

In this study, the Steady-State Water Chemistry (SSWC) model embedded into the First-order Acidity Balance (FAB) model (Henriksen and Posch, 2001; UBA, 2004) was used to calculate critical loads for 18 ICP IM catchments for which observations of runoff volume and water chemistry were available for the years evaluated (Fig. 1, Table 1). This is an extension of previous work, which calculated critical loads of acidification for 16 ICP IM catchments using the SSWC model only (Holmberg et al. 2010). Mean values of observed concentrations (sulphate, nitrate, calcium, magnesium, potassium, sodium, chloride) for the period 2000-2002 were used in the calculations.

In the FAB model, critical loads of N and S acidity are derived in the same way as in the Simple Mass Balance model, widely used for computing soil critical loads (Sverdrup and De Vries, 1994; UBA, 2004). Starting from the charge balance in the lake or stream water and using steady-state mass balances of N, S and base cations, one arrives at the following equation (Henriksen and Posch, 2001):

(1) $$(1-\rho_S)\cdot S_{dep}+(1-\rho_N)\cdot b_N\cdot N_{dep}=(1-\rho_N)\cdot M_N+L_{crit},$$

where $\rho_S$ and $\rho_N$ represent in-lake retention of S and N, and $L_{crit}$ is the difference between the net base cation leaching and the critical ANC leaching.

Every pair ($N_{dep}$, $S_{dep}$) of N and S deposition fulfilling this equation is called a critical load of acidity of that catchment. The dimensionless coefficient $b_N$ and the flux $M_N$ depend on $N_{dep}$: If $N_{dep} \leq N_u+N_i$, i.e. the N deposition is smaller than the sum of net uptake $N_u$ and net immobilization $N_i$ of N in the terrestrial catchment, then $M_N = 0$ and $b_N = r$, where $r$ is the lake-to-catchment area ratio, reflecting the fact that only the N deposited directly onto the lake contributes to leaching. If, however, $N_{dep} > N_u+N_i$, then $M_N = (1–f_{de})\cdot(1–r)\cdot(N_u+N_i)$ and $b_N = 1–(1–r)\cdot f_{de}$, where $f_{de}$ is the fraction of N input denitrified. The critical loads of acidity define a trapezoidally-shaped function in the ($N_{dep}$, $S_{dep}$)-plane, called the critical load function (see Figure 2), defined by the maximum critical load of S, $CL_{max}S$ (if $N_{dep} = 0$) and the maximum critical load of N, $CL_{max}N$ (for $S_{dep} = 0$).

It was assumed that there is no permanent removal of biomass from the integrated monitoring sites as they are located in protected areas with no significant management. Therefore the rate of net nitrogen uptake $N_u$ from the soil was set to zero at all sites, since nitrogen incorporated into growing vegetation was considered to be balanced, in the long term, by nitrogen released from decaying litter. A constant N immobilization in the catchment soils of $N_i = 0.5$ kg N $ha^{-1}a^{-1}$ was used (UBA, 2004). The denitrification fraction in the catchment soils was estimated as $f_{de} = 0.1+0.7\cdot f_{peat}$, where $f_{peat}$ is the fraction of peatlands in the terrestrial catchment (after Posch et al., 1997). The values of $f_{peat}$ are given in Table A1 of the Supplementary material. The dimensionless quantities $\rho_N$ and $\rho_S$ account for the in-lake retention of N and S respectively. The retention factor for N is modelled following Kelly et al. (1987): $\rho_N = s_N/(s_N+Q/r)$, where $s_N$ is the net mass transfer coefficient. A value of $s_N = 6.5$ m $yr^{-1}$ was chosen for all lakes using data from Kaste and Dillon (2003). An analogous equation describes $\rho_S$, and $s_S = 0.5$ m $yr^{-1}$ was used for all lakes (after Baker and Brezonik, 1988).

The term $L_{crit}$ in the critical load equation denotes the difference between the net base cation leaching and the critical ANC leaching. Since the base cation fluxes, especially those due to weathering in the catchment soils, are poorly known, this term is modelled by the SSWC model (Henriksen and Posch, 2001), i.e.:

$$L_{crit} = Q\cdot([BC^*]_0 – [ANC]_{limit}), \quad (2)$$

from catchment runoff $Q$ (m $yr^{-1}$), pre-acidification non-marine concentration of base cations $[BC^*]_0$ (μeq $L^{-1}$) (BC=Ca+Mg+K+Na) and a critical acid neutralizing capacity $[ANC]_{limit}$ (μeq $L^{-1}$). The criterion is the lowest acid neutralizing capacity that does not damage target biota (fish). The value $[ANC]_{limit} = 20$ μeq $L^{-1}$ was used in this study (Lien et al., 1996). The pre-acidification base cation concentration is calculated as (Henriksen and Posch, 2001):

$$[BC^*]_0 = [BC^*] – F\,([SO_4^*] – [SO_4^*]_0 + [NO_3]\,), \quad (3)$$

where the pre-acidification concentration of sulphate is estimated as $[SO_4^*]_0 = a + b\cdot[BC^*]$, with $a = 8$ μeq $L^{-1}$, $b = 0.17$, and the so-called F-factor is computed as (Brakke et al., 1990):

$$F = \sin(\pi/2[BC^*]/[S]), \quad (4)$$

with $[S] = 400$ μeq $L^{-1}$.

## 2.2 Critical loads for eutrophication

Deposition of nitrogen may have an impact on sensitive ecosystems through multiple pathways, including accumulation of N compounds, resulting in changes of species composition and reduction in plant diversity as well as increased susceptibility to secondary stress and disturbance factors such as drought, frost, pathogens or herbivores (Achermann and Bobbink, 2003; Phoenix et al., 2006; Nordin et al., 2006; Salemaa et al., 2008; Bobbink and Hettelingh, 2011; Pardo et al., 2011).

Mass balance critical loads of nutrient nitrogen $CL_{nut}N$ (eq $ha^{-1}yr^{-1}$) were calculated for the same 18 catchments for which observations of runoff volume and water chemistry were available for the evaluated years (Fig. 1). Critical loads of nutrient nitrogen were calculated with an N budget equation that describes the amount of N deposition the terrestrial ecosystem may receive without increasing the soil solution N concentration above a specified limit $[N]_{acc}$

$$CL_{nut}N = N_i + N_u + Q\,[N]_{acc} \;/\; (1 - f_{de}), \quad (5)$$

where $N_i$ is the long-term net immobilisation of N in the soil, $N_u$ is the net removal of N in harvested vegetation, $f_{de}$ is the fraction of N input denitrified and $Q$ the annual runoff (see above). The acceptable N concentration $[N]_{acc}$ in soil leachate is set to avoid nutrient imbalances or vegetation changes, (UBA 2004, De Vries et al. 2007). In this study, site-specific values for $[N]_{acc}$ (0.3 to 5.2 mgN $L^{-1}$) were chosen to reflect the sensitivity of part of the vegetation of the site (Table A1, supplementary material).

In addition to the above mass balance critical loads of nutrient N, empirical critical loads of nutrient N, $CL_{emp}N$, were also assigned to a total of 83 vegetation plots at 37 IM sites (Fig. 1). This was based on the work by Bobbink and Hettelingh (2011), who reported critical loads of nutrient N from extensive empirical studies on the response of natural and semi-natural ecosystems to N deposition. The empirical critical loads of N are given for the groups of natural and semi-natural ecosystems, which have been classified according to the EUNIS (European Nature Information System) habitat classification for Europe (Davies et al., 2004). On the basis of information on the vegetation reported for the plots of the Integrated Monitoring sites, the individual plots were classified into EUNIS classes. For each EUNIS class the empirical critical load was set to the minimum of the range proposed by Bobbink and Hettelingh (2011). In this analysis, site-specific factors that modify the empirical values were not considered, in contrast to the practice of some of the individual countries in their reporting to the CCE; e.g. in the UK, the reported empirical critical loads vary with the amount of rainfall (Hall et al., 2011). The values of the $CL_{emp}N$ range from 5 to 15 kg N $ha^{-1}yr^{-1}$ (360 to 1070 eq $ha^{-1}yr^{-1}$) (Table A1, Supplementary material).

## 2.3 Deposition estimates and critical load exceedances

The deposition estimates were generated with the source-receptor matrices – derived from the EMEP/MSC-W unified atmospheric dispersion model (EMEP 2010) – used in integrated assessment under the LRTAP Convention (Amann et al. 2010) using the NAT2000, COB2020, Low*2020, MID2020, High*2020 and MFR2020 emission scenarios. The NAT2000 scenario represents historic emissions for the year 2000 and the COB2020 scenario national economic projections for 2020 as reported by the countries under the LRTAP Convention. The Low*2020 and High*2020 scenarios refer to the ambition level of the reductions, so that with lower reductions the scenario Low*2020 leads to more deposition than High*2020. The Low*2020, MID2020 and High*2020 scenarios are based on economic projections by the PRIMES model for the year 2020,

and MFR2020 assumes all available abatement technologies being implemented by 2020. The depositions were available for 50×50km$^2$ grid cells covering Europe.

The increased risk for harmful effects is quantified by the exceedance of a critical load. For nutrient N critical loads, the exceedance is defined as the difference between the N deposition and the critical load value. Negative exceedance values (for sites where the critical loads are not exceeded) are included in graphs in order to show the difference between deposition and critical load value for all cases.

In the case of acidification, both N and S contribute to the exceedance, and there are, in general, infinitely many ways of reducing deposition so that the critical loads are no longer exceeded. It has become customary to define the exceedance as the sum of the N and S deposition reduction required to reach the critical load function on the shortest path (Posch et al., 2001; UBA, 2004): $Ex(N_{dep},S_{dep}) = \Delta N+\Delta S$ (see Figure 2). If $(N_{dep},S_{dep})$ lies below the critical load function, the critical loads are not exceeded.

For empirical critical loads of nutrient N, a site was considered protected from eutrophication if all the vegetation habitats within the site were protected ($N_{dep}$ lower than $CL_{emp}N$). For each site, the exceedance of $CL_{emp}N$ was calculated as a habitat-specific area-weighted average value. Exceedance averages were calculated as arithmetic means of the positive exceedance values over the number of sites at which the critical loads were exceeded ($AExCL_A$, $AExCL_{nut}N$, $AExCL_{emp}N$, all in eq ha$^{-1}$ yr$^{-1}$).

## 2.4 Empirical impact indicators

For the study of chemical empirical impact indicators in relation to exceedance of critical loads of acidification ($ExCL_A$), 17 catchments were selected (Table 1). The selection of catchments was guided by the availability of surface water chemistry and runoff data in the ICP IM database. At these same catchments, the mass balance critical loads of nutrient N ($ExCL_{nut}N$) were compared with fluxes of total inorganic nitrogen (TIN = $NO_3^-$+$NH_4^+$) (Table 2). In addition, the empirical critical loads of nutrient N ($ExCL_{emp}N$) were investigated in relation to observed monitoring results (empirical impact indicators) at a total of 24 sites, in which surface water concentration data of TIN were available (Table 2). A list of the National Focal Points contributing runoff chemistry data is available at the web site of the ICP IM (ICP IM network, 2011).

The exceedances of critical loads were computed with the historical deposition estimates NAT2000. To compare catchment responses with exceedances of critical loads at the IM catchments, the annual average (2000 – 2002) runoff water fluxes and concentrations of the key acidification parameters acid neutralising capacity ANC, hydrogen-ion ($H^+$) and non-marine sulphate ($xSO_4$), and eutrophication parameter TIN were used as empirical impact indicators. Acid neutralising capacity ANC was calculated as ($Ca^{2+}$+$Mg^{2+}$+$Na^+$+$K^+$) – ($SO_4^{2-}$+$Cl^-$+$NO_3^-$). The period 2000-2002 was used to be consistent with the deposition estimates (NAT2000). Annual runoff water element fluxes were calculated by summing mean monthly fluxes, obtained from monthly mean water flux and monthly mean solute concentration. Methods for collection, storage and analysis are described in the ICP IM Manual (1998).

The empirical impact indicators were compared with critical load exceedances by correlation analysis. The correlation of runoff water concentrations and fluxes on the exceedances of critical loads was examined using non-parametric Kendall-tau correlation analysis (Conover, 1980). The

sites BY02, DE01 and EE02 were excluded from the comparison between exceedance of critical load of N and TIN runoff water chemistry. High concentrations and fluxes of TIN at sites BY02 and EE02 are due to inputs of N from agriculture, and for site DE01 due to excess mineralization after Norway spruce (*Picea abies*) dieback due to a bark beetle attack in 1996-1997, and are therefore not considered representative of the effect of N deposition.

## 3. Results and discussion

### 3.1 Acidification

The ICP IM catchments vary in their sensitivity to acidification. Based on the surface water chemistry, 4 out of 18 sites can be characterized as acid-sensitive (ANC $\leq$ 20 µeq $L^{-1}$), and for these sites the critical load of acidity was exceeded in 2000. The acid-sensitive sites are also characterized by high acidity (pH < 5) of the surface water. Surface waters with an ANC over 200 µeq $L^{-1}$, on the other hand, are considered to be insensitive to acidification, and this is the case for about 40% of the sites (Table 1).

More than half of the sites were protected from surface water acidification in 2000; 11 sites out of 18, or 61% (Tables 1, 3). For all deposition scenarios in 2020, 12 sites (67%) were protected from acidification. Even the high ambition High*2020 or MFR2020 scenarios would not protect the remaining 6 sites: CZ01, CZ02, NO01, SE04, SE14, SE15. Arithmetic averages were calculated for the exceedance of critical loads of acidity for the sites that were not protected from acidification (7 in 2000; 6 in 2020). The average exceedance (for the exceeded sites only) decreased from 987 eq $ha^{-1}$ $yr^{-1}$ in 2000 to 310 eq $ha^{-1}$ $yr^{-1}$ in 2020, for the maximum feasible reductions MFR2020 scenario (Table 3).

There was good correlation between the exceedances of acidity critical loads ($ExCL_A$) and key acidification parameters in runoff water, both in annual mean fluxes and concentrations (Fig. 3, Table 4). At the most acidified or acid-sensitive sites (in terms of low ANC and high $H^+$ concentrations and fluxes), the sulphur deposition exceeded critical loads for acidification to a higher degree than at other, less sensitive sites. At lower deposition levels, these sites were closer to the exceedance threshold than the sensitive sites. The correlation between sulphate and $ExCL_A$ among the IM sites was poorer, due to differences in soil susceptibility to acidification. Some sites (EE02, LT01, LT03, LV01, LV02) are located in deep calcareous soils with high initial concentrations of sulphate, calcium and magnesium, and high concentrations of ANC ( > 1000 µeq $L^{-1}$, n=9), and are therefore well protected against acidification (Table 1). Among the acid-sensitive sites (ANC < 100 µeq $L^{-1}$) $ExCL_A$ increases with increasing sulphate flux (Kendall $\tau$ b correlation coefficient 0.67, $p < 0.05$) (Fig. 4).

Much has been achieved in reducing European emissions of S (and to a lesser extent N) during the last decades. Between 1990 and 2009, European emissions of $SO_x$, $NO_x$ and $NH_3$ have been reduced by 73 %, 36 % and 31 %, respectively (Fagerli et al., 2011). The resulting decreases in acidifying deposition, and consequently reduced CL exceedances, have led to well-documented recovery in ecosystems, regarding both chemical (e.g. Stoddard et al., 1999; Evans et al., 2001; Wright et al., 2005) and to a lesser extent biological indicators (e.g. Snucins et al., 2001; Skjelkvåle and de Wit, 2011). Dynamic model calculations show that further improvements are likely to occur if the planned reductions are implemented (Aherne et al., 2008; Larssen et al., 2010, Oulehle et al., 2012).

### 3.2 Eutrophication

At 14 IM sites of 18 examined in this study, the mass balance critical load of nutrient nitrogen ($CL_{nut}N$) was exceeded in 2000 (NAT2000) (Tables 2, 3), i.e. only 4 sites (22%) were protected from eutrophication in 2000. In 2020 the current reduction plans COB2020 and the low ambition Low*2020 scenarios would protect 5 sites, while the high ambition High*2020 and the MFR scenario would protect 7 sites from eutrophication. The average exceedance of the mass balance critical load of nutrient nitrogen was 625 eq $ha^{-1}$ $yr^{-1}$ or 8.8 kg N $ha^{-1}$ $yr^{-1}$ in 2000 and 230 eq $ha^{-1}$ $yr^{-1}$ or 3.2 kg N $ha^{-1}$ $yr^{-1}$ in 2020 under the MFR scenario N deposition (Table 2).

From the perspective of using the empirical critical loads of nitrogen ($CL_{emp}N$) as an indicator of nitrogen tolerance, 7 sites of 37 (19%) were protected from eutrophication in 2000 (Tables 2, 3). In 2020, the mid and high ambition scenarios protected 15 sites, whereas 20 sites would be protected if all available abatement technologies were implemented (MFR). The average exceedance of the empirical critical load of nitrogen was 578 eq $ha^{-1}$ $yr^{-1}$ or 8.1 kg N $ha^{-1}$ $yr^{-1}$ in 2000 and 154 eq $ha^{-1}$ $yr^{-1}$ or 2.2 kg N $ha^{-1}$ $yr^{-1}$ in 2020 under the MFR scenario N deposition (Table 3).

There was good agreement between exceedances of critical loads of nitrogen and observed N leaching (Table 4, Fig. 5). The ICP IM sites where the empirical critical load of nutrient nitrogen ($CL_{emp}N$) was exceeded showed higher TIN concentrations and fluxes in runoff. With the NAT2000 deposition scenario, the empirical critical load of nutrient nitrogen ($CL_{emp}N$) was exceeded at 18 (75%) sites of those for which TIN concentrations were available (24 sites). For those 17 sites where TIN fluxes were available, $CL_{emp}N$ was exceeded at 14 sites (82 %) (Fig. 5). The concentrations and fluxes of TIN increased with increasing critical load exceedance also regarding mass balance nutrient N critical loads ($CL_{nut}N$).

Empirical data from forested ecosystems in Europe show a clear relationship between N deposition and N leaching (Dise and Wright, 1995, Wright et al., 2001, MacDonald et al., 2002, Kaste et al., 2007). Dise and Wright (1995) and Wright et al. (2001) observed low concentrations of nitrate in stream water at sites with less than 10 kg N $ha^{-1}$ $yr^{-1}$ deposition, elevated concentrations at sites receiving more than 25 kg N $ha^{-1}$ $yr^{-1}$ and variable responses in the mid-range. In our study, N deposition was less than 25 N $ha^{-1}$ $yr^{-1}$ at all catchments and $NO_3$-N constituted on average 79% of the TIN in stream water 2000-2002. The highest TIN fluxes were observed at catchments receiving more than 7 kg N $ha^{-1}$ $yr^{-1}$ in deposition (Fig. 6).

In contrast to sulphur, nitrogen is much more influenced by biological processes within ecosystems, and most of the N deposition is usually retained in forest ecosystems; typically < 10% is leached in runoff of boreal forest ecosystems, mostly as $NO_3$ (e.g. Wright et al., 2005). Furthermore, increasing temperature and availability of both $CO_2$ and N have stimulated forest growth (Spiecker et al., 1996) and N uptake from the soils (Johnson, 2006). Hence changes in N deposition may not always directly correlate with changes in inorganic N leaching. The variation in the relationship between N concentrations and fluxes and exceedances of critical loads may be expected, since N leaching depends on landscape characteristics, site history, soil fertility and organic matter pool, vegetation type and hydrological processes (Helliwell et al., 2007; Rothwell et al., 2008). However, continued high N deposition may result in N saturation of terrestrial ecosystems in the long run and excess $NO_3$ leaching to surface waters (e.g. Aber et al., 1989, Dise and Wright, 1995, MacDonald et al., 2002). There are still large uncertainties regarding the processes controlling N retention in ecosystems, and further research is required to narrow them down.

As time is not a variable in critical load calculations, critical loads represent the threshold beyond which effects on the ecosystems might occur, without regard to the time frame in which the effects might appear. Critical loads represent a static view of ecosystems, while in reality changing climate,

growing vegetation, and accumulation and release of elements into soil and organic matter, lead to dynamic responses of the ecosystems to changing deposition levels. A site could be exceeded but not yet damaged, or no longer exceeded but not yet recovered. Dynamic models are used to study these and other aspects (e.g. Jenkins et al., 2003, Hettelingh et al., 2007). In this paper we have compared exceedances of steady-state critical loads with empirical impact indicator observations as a snapshot of dynamically changing ecosystems. The comparison is relevant and our results provide evidence on the link between critical loads and empirical impacts. The coincidence of exceedance with effects is, however, neither a sufficient nor necessary condition for the validation of critical loads.

## 4. Conclusions

Although much has been achieved with regard to the reduction of acidifying deposition, only 61% of the ICP IM catchments studied here were protected from acidification in 2000 and emission reductions envisaged for 2020 would increase the level of protection to only 67 %. For eutrophication, the situation is more severe, only about 20% of the catchments were protected in 2000 and 39 % or 54 % would be protected in 2020, depending on whether mass balance or empirical critical loads of N are considered.

Empirical impact indicators as derived from observations at ICP IM catchments were in good agreement with exceedances of critical loads of acidification and eutrophication. Data from the ICP IM thus provide evidence of a connection between modelled critical loads and empirical monitoring results for acidification parameters and nutrient nitrogen. This increases the confidence in the European-scale critical loads mapping used in integrated assessment modelling.

## Role of sponsor

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## Tables and Figures

Table 1. Exceedances of critical loads for acidification ($ExCL_A$) according to the historic scenario NAT2000 and mean annual concentrations and fluxes (2000-2002) of ANC, $H^+$, non-marine x(Ca+Mg) and $xSO_4$ in runoff water at 18 IM catchments. Negative exceedance values indicate that the critical loads are not exceeded. Runoff volume observations were not available at site AT01 (n.d.).

| Site code | $ExCL_A$ (eq $ha^{-1}yr^{-1}$) | ANC | $H^+$ | x(Ca+Mg) | $xSO_4$ | ANC | $H^+$ | x(Ca+Mg) | $xSO_4$ |
|---|---|---|---|---|---|---|---|---|---|
| | | Concentration (µeq $L^{-1}$) | | | | Flux (eq $ha^{-1}$ $yr^{-1}$) | | | |
| AT01 | -14160 | 3714 | 0.05 | 3871 | 64 | n.d. | n.d. | n.d. | n.d. |
| CZ01 | 1500 | 443 | 0.10 | 1282 | 1162 | 311 | 0.07 | 810 | 723 |
| CZ02 | 2097 | -31 | 61 | 143 | 256 | -198 | 411 | 783 | 1427 |
| DE01 | -241 | 126 | 0.84 | 198 | 63 | 1326 | 15 | 2423 | 849 |
| EE02 | -9204 | 2875 | 0.04 | 3055 | 311 | 2675 | 0.03 | 2930 | 333 |
| FI01 | -206 | 67 | 28 | 171 | 140 | 146 | 66 | 374 | 299 |
| FI03 | -676 | 124 | 0.50 | 96 | 25 | 387 | 1.9 | 300 | 81 |
| GB01 | 40 | 56 | 0.43 | 43 | 27 | 274 | 4.6 | 225 | 149 |
| LT01 | -2074 | 2563 | 0.03 | 3829 | 1274 | 1507 | 0 | 2261 | 758 |
| LT03 | -1531 | 1015 | 0.09 | 1846 | 837 | 796 | 0.23 | 1985 | 1161 |
| LV01 | -5408 | 2388 | 0.05 | 2940 | 515 | 3431 | 0.12 | 4161 | 662 |
| LV02 | -7380 | 2258 | 0.06 | 2531 | 311 | 5019 | 0.13 | 5706 | 754 |
| NO01 | 1001 | -17 | 18 | 30 | 52 | -346 | 304 | 286 | 666 |
| NO02 | -371 | 37 | 0.53 | 39 | 9.7 | 626 | 13 | 687 | 141 |
| SE04 | 1187 | -3.6 | 50 | 28 | 51 | -29 | 299 | 206 | 371 |
| SE14 | 583 | 82 | 31 | 136 | 126 | 213 | 112 | 477 | 513 |
| SE15 | 497 | -20 | 29 | 42 | 110 | -150 | 188 | 223 | 650 |
| SE16 | -213 | 86 | 3.2 | 79 | 42 | 424 | 26 | 388 | 199 |

Table 2. Exceedances of critical loads of nutrient nitrogen $ExCL_{nut}N$ and exceedances of empirical values of critical loads of nitrogen $ExCL_{emp}N$ and mean annual (2000-2002) concentrations and fluxes of TIN ($NO_3$ + $NH_4$) in runoff water at IM catchments. Negative exceedance values indicate that the critical loads are not exceeded. Runoff observations were not available at all sites (n.d.).

| Site code | $ExCL_{nut}N$ (eq $ha^{-1}yr^{-1}$) | $ExCL_{emp}N$ (eq $ha^{-1}yr^{-1}$) | TIN (µeq $L^{-1}$) | TIN (eq $ha^{-1}yr^{-1}$) |
|---|---|---|---|---|
| Number of sites | 18 | 37 | 24 | 17 |
| AT01 | 1117 | 710 | 101 | n.d. |
| BY02 | n.d. | 42 | 85 | n.d. |
| CZ01 | 1114 | 763 | 87 | 62 |
| CZ02 | 1172 | 831 | 4.2 | 29 |
| DE01 | 1140 | 902 | 103 | 1373 |
| DE02 | n.d. | 736 | 12 | n.d. |
| EE01 | n.d. | 804 | 45 | n.d. |
| EE02 | 189 | -144 | 71 | 71 |
| FI01 | 56 | 42 | 5.7 | 13 |
| FI03 | -108 | -101 | 1.6 | 5.7 |
| FI04 | n.d. | -191 | 0.9 | n.d. |
| FI05 | n.d. | -283 | 1.0 | n.d. |
| GB01 | -739 | 115 | 1.6 | 9.5 |
| GB02 | n.d. | 3 | 22 | n.d. |
| IS01 | n.d. | -510 | n.d. | n.d. |
| IT01 | n.d. | 556 | n.d. | n.d. |
| IT02 | n.d. | 556 | n.d. | n.d. |
| IT03 | n.d. | 1257 | n.d. | n.d. |
| IT05 | n.d. | 551 | n.d. | n.d. |
| IT06 | n.d. | 103 | n.d. | n.d. |
| IT07 | n.d. | 1974 | n.d. | n.d. |
| IT08 | n.d. | 1368 | n.d. | n.d. |
| IT09 | n.d. | 391 | n.d. | n.d. |
| IT10 | n.d. | 703 | n.d. | n.d. |
| IT11 | n.d. | 657 | n.d. | n.d. |
| IT12 | n.d. | 653 | n.d. | n.d. |
| IT13 | n.d. | 806 | n.d. | n.d. |
| LT01 | 465 | 383 | 11 | 7.4 |
| LT03 | 699 | 653 | 17 | 27 |
| LV01 | 680 | 523 | 30 | 54 |
| LV02 | 275 | 222 | 13 | 32 |
| NO01 | 442 | 498 | 9.2 | 116 |
| NO02 | -408 | -108 | 2.2 | 36 |
| SE04 | 660 | 329 | 3.7 | 27 |
| SE14 | 534 | 53 | 5.5 | 19 |
| SE15 | 210 | 157 | 2.0 | 11 |
| SE16 | -99 | -166 | 1.6 | 5.7 |

Table 3. Average exceedances for sites not protected from acidification (AExCL) and eutrophication ($AExCL_{nut}N$, $AExCL_{emp}N$ ) and percentage of sites protected with different deposition scenarios.

| | Total nr of sites | NAT2000 | COB2020 | Low*2020 | MID2020 | High*2020 | MFR2020 |
|---|---|---|---|---|---|---|---|
| $AExCL_A$ (eq $ha^{-1}yr^{-1}$) | 18 | 987 | 494 | 421 | 392 | 354 | 310 |
| Acidification protection % | 18 | 61 % | 67 % | 67 % | 67 % | 67 % | 67 % |
| $AExCL_{nut}N$ (eq $ha^{-1}yr^{-1}$) | 18 | 625 | 369 | 284 | 286 | 277 | 230 |
| Eutrophication protection % mass balance critical load | 18 | 22 % | 28 % | 28 % | 33 % | 39 % | 39 % |
| $AExCL_{emp}N$ (eq $ha^{-1}yr^{-1}$) | 37 | 578 | 349 | 238 | 221 | 177 | 154 |
| Eutrophication protection % empirical critical load | 37 | 19 % | 35 % | 38 % | 41 % | 41 % | 54 % |

Table 4. Correlations (Kendall Tau b correlation coefficients) of mean annual (2000-2002) concentrations and fluxes for ANC, $xSO_4$, $H^+$and TIN with exceedances of critical load for acidification ($ExCL_A$, NAT2000 scenario), exceedances of critical load of mass balance nutrient nitrogen ($ExCL_{nut}N$, NAT2000 scenario) and empirical critical load of nutrient nitrogen ($ExCL_{emp}N$, NAT2000 scenario). Statistically significant correlations ($p < 0.05^{*}$, $p < 0.01^{**}$, $p < 0.001^{***}$) are highlighted in bold.

| | ANC Mean Conc. | ANC Mean Flux | $xSO_4$ Mean Conc. | $xSO_4$ Mean Flux | $H^+$ Mean Conc. | $H^+$ Mean Flux | TIN Mean Conc. | TIN Mean Flux |
|---|---|---|---|---|---|---|---|---|
| $ExCL_A$ | **-0.67**$^{***}$ | **-0.72**$^{***}$ | -0.06 | 0.13 | **0.69**$^{***}$ | **0.66**$^{***}$ | -0.18 | 0.16 |
| $ExCL_{nut}N$ | 0.11 | -0.03 | **0.39*** | **0.71**$^{***}$ | 0.08 | 0.09 | **0.55**$^{**}$ | **0.39**$^{*}$ |
| $ExCL_{emp}N$ | -0.04 | -0.10 | **0.32**$^{*}$ | **0.66**$^{***}$ | 0.13 | 0.07 | **0.56**$^{***}$ | **0.43**$^{*}$ |

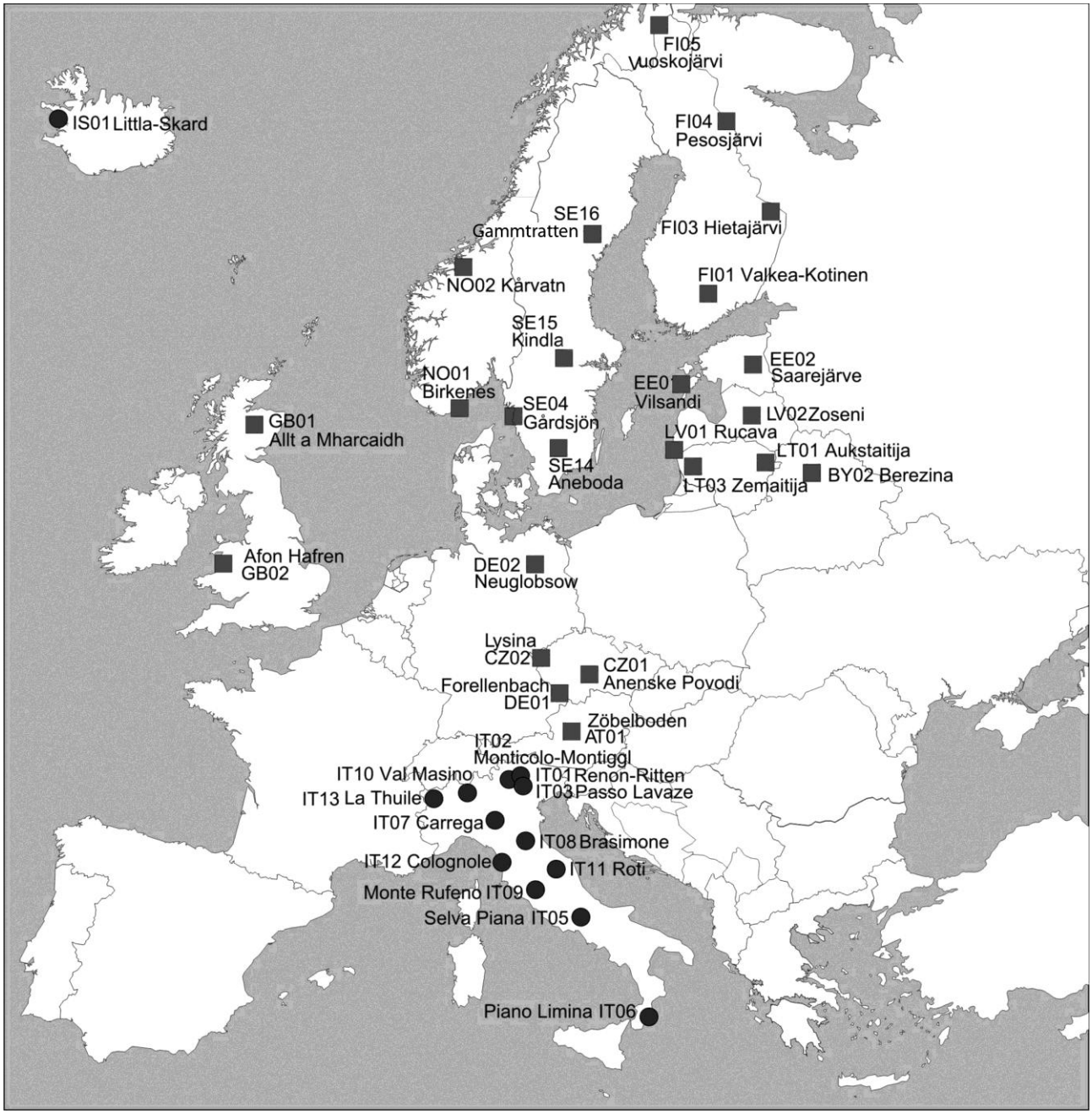


Figure 1. Location of the 37 ICP IM sites included in the critical load calculations. The catchments included in the comparison between exceedances of critical loads and runoff water concentrations and fluxes are indicated with a square (■).

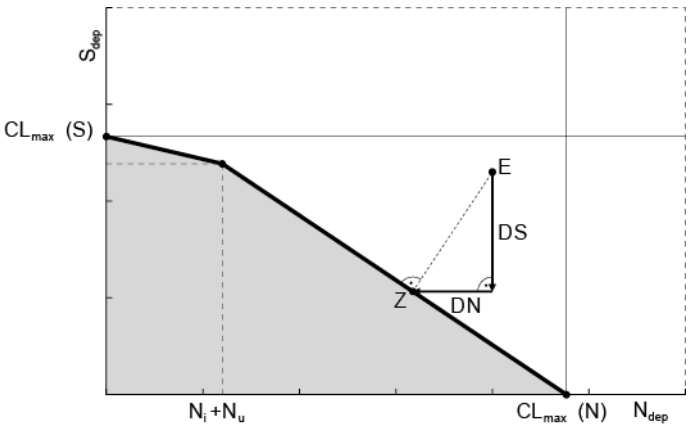


Figure 2. Piece-wise linear critical load function (CLF) of acidifying N and S for a lake or stream as defined by its catchment properties. For a given deposition pair ($N_{dep}$,$S_{dep}$) the critical load exceedance is calculated by adding the N and S deposition reductions needed to reach the CLF via the shortest path (E→Z): Ex = ΔS+ΔN. The grey area below the CLF denotes deposition pairs for which the critical loads are not exceeded.

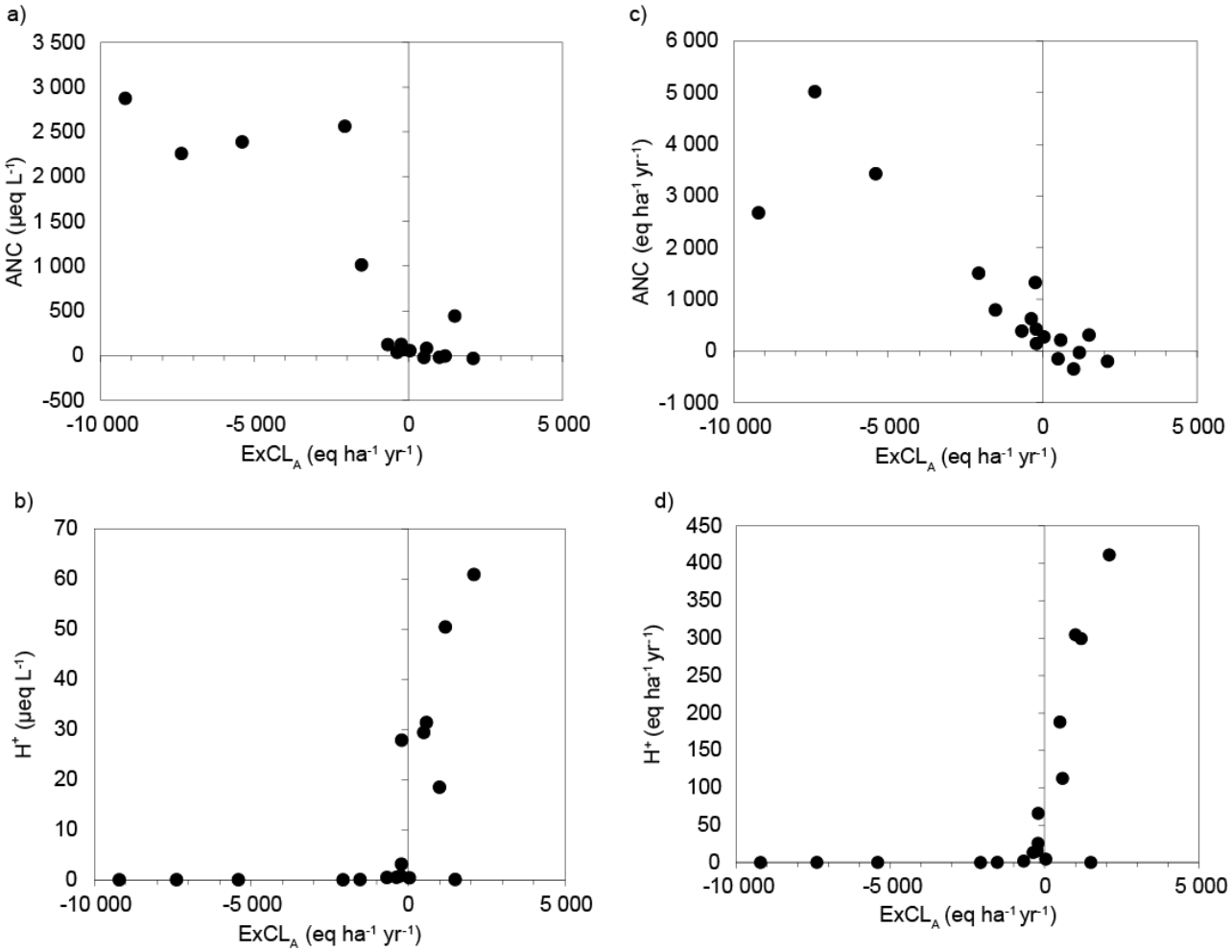


Figure 3. Acidification empirical impact indicators in relation to exceedance of critical loads. The x-axes show exceedance of critical load for acidification ($ExCL_A$, NAT2000 scenario) for aquatic ecosystems. The y-axes show annual mean concentrations (a, b) and fluxes (c, d) measured between 2000 and 2002 of ANC and $H^+$ in runoff for 18 ICP IM sites. Negative exceedance values indicate that the critical loads are not exceeded.

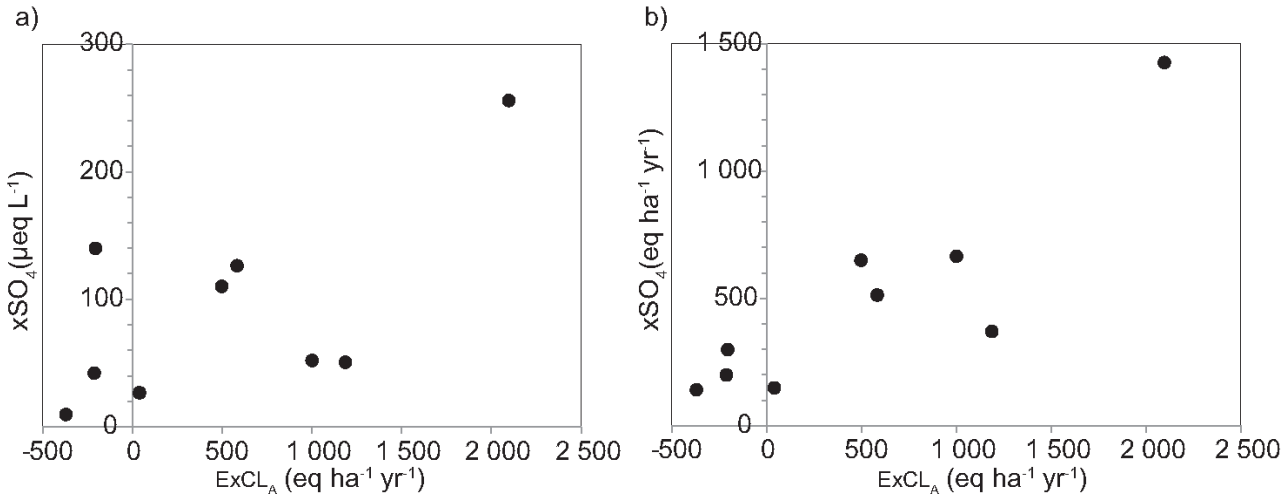


Figure 4. Acidification empirical impact indicators in relation to exceedance of critical loads at acid-sensitive catchments. The x-axes show exceedance of critical load for acidification ($ExCL_A$, NAT2000 scenario) for aquatic ecosystems at 9 acid-sensitive ICP IM catchments with ANC < 100 µeq $L^{-1}$. The y-axes show annual mean concentrations (a) and fluxes (b) of non-marine sulphate ($xSO_4$) measured between 2000 and 2002. Negative exceedance values indicate that the critical loads are not exceeded.

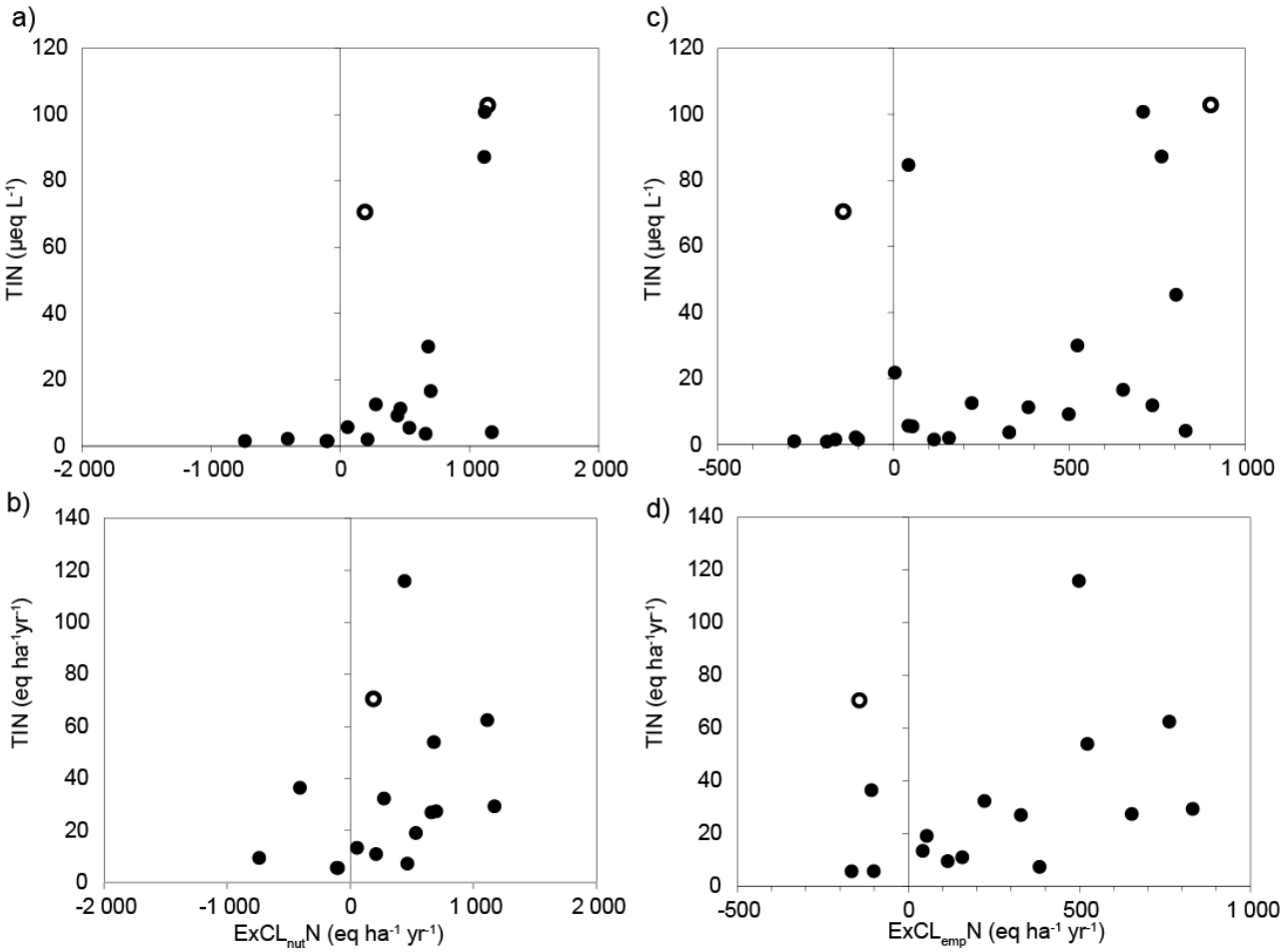


Figure 5. Eutrophication empirical impact indicators in relation to exceedance of critical loads of N. The x-axes show exceedances of mass balance critical loads of nutrient N ($ExCL_{nut}N$, NAT2000 deposition, a, b) and exceedances of empirical critical loads of nutrient N ($ExCL_{emp}N$, NAT2000 deposition, c, d). The y-axes show annual mean concentrations (a, c) and fluxes (b, d) measured (2000-2002 average) of TIN (=$NO_3$+$NH_4$) in runoff. Negative exceedance values indicate that the critical loads are not exceeded. Open circles indicate catchments with inputs of N from sources other than deposition. TIN flux for DE01 (1373 eq $ha^{-1}$ $yr^{-1}$) is outside axis range and not shown in graphs.

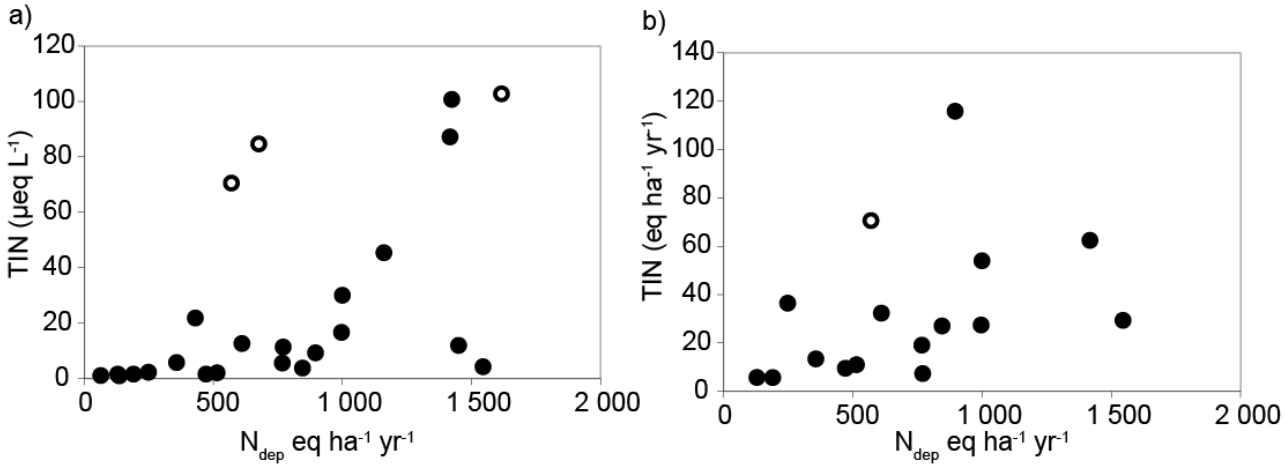


Figure 6. TIN in relation to N deposition. The x-axes show N depositions (NAT2000 scenario) and the y-axes annual mean concentrations of TIN (=$NO_3$+$NH_4$) measured between 2000 and 2002 at 24 ICP IM sites (a) and annual mean fluxes of TIN measured between 2000 and 2002 at 16 ICP IM sites (b). Open circles indicate sites with inputs of N from sources other than deposition. The TIN flux for DE01 (1373 eq $ha^{-1}$ $yr^{-1}$) is outside axis range and thus not shown.

Table A1. Properties of ICP IM catchments and vegetation plots as well as parameters used in the calculation of mass balance critical loads and empirical critical load values. Total catchment area (ha), area of lake (ha), fraction of peatland of terrestrial catchment area $f_{peat}$, acceptable concentration of N in soil solution $N_{acc}$ (mg $L^{-1}$), predominant vegetation per plot, area of vegetation plot (ha), EUNIS code, and empirical critical load of N $CL_{emp}N$ (kg $ha^{-1}$ $yr^{-1}$).

| **Site** | | **Total area (ha)** | **Lake area (ha)** | $f_{peat}$ | $N_{acc}$ (mg $L^{-1}$) | **Predominant Vegetation per Plot** | **Plot Area (ha)** | **EUNIS code** | $CL_{emp}N$ (kg $ha^{-1}$ $yr^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|
| AT01 | Zöbelboden | 90 | 0 | 0 | 0.3 | Spruce (*Picea abies*) | 45 | G3.1 | 10 |
| | | | | | | Beech (*Fagus sylvatica*) | 45 | G4 | 10 |
| BY02 | Berezina br. | 72 600 | -[a] | -[a] | -[a] | Boggy meadow | 8 494 | D1 | 5 |
| | | | | | | Coniferous forest | 60 476 | G4 | 10 |
| CZ01 | Anenske povodi | 268 | 0 | 0 | 5.2 | Alder (*Alnus*) | 2.9 | G1 | 10 |
| | | | | | | Ash (*Fraxinus excelsior*) | 1.1 | G1 | 10 |
| | | | | | | Beech (*Fagus sylvatica*) | 5.4 | G1 | 10 |
| | | | | | | Birch (*Betula*) | 1.1 | G1 | 10 |
| | | | | | | Larch (*Larix decidua*) | 4 | G1 | 10 |
| | | | | | | Lime (*Tilia*) | 0.3 | G1 | 10 |
| | | | | | | Maple (*Acer*) | 0.3 | G1 | 10 |
| | | | | | | Oak (*Quercus*) | 0.3 | G1 | 10 |
| | | | | | | Poplar (*Populus*) | 0.5 | G1 | 10 |
| | | | | | | Norway spruce (*Picea abies*) | 205 | G3.1 | 10 |
| | | | | | | Douglas fir (*Pseudotsuga menziezii*) | 0.3 | G3.1 | 10 |
| | | | | | | Fir (*Abies alba*) | 1.9 | G3.1 | 10 |
| | | | | | | Pine (*Pinus sylvestris*) | 45 | G3.4 | 5 |
| CZ02 | Lysina | 27 | 0 | 0 | 0.8 | Norway spruce (*Picea abies*) | 19 | G3.1 | 10 |
| | | | | | | Norway spruce (*Picea abies*) | 8 | G3.1 | 10 |
| DE01 | Forellenbach | 69 | 1.4 | 0 | 0.5 | Beech (*Fagus sylvatica*) | 21 | G1 | 10 |
| | | | | | | Spruce (*Picea abies*) | 48 | G3.1 | 10 |
| DE02 | Neuglobsow | 2 140 | - | - | - | Beech (*Fagus sylvatica*) and pine (*Pinus sylvestris*) | 2 140 | G4 | 10 |
| EE01 | Vilsandi | 0.8 | - | - | - | Scots pine (*Pinus sylvestris*) | 0.8 | G3.4 | 5 |
| EE02 | Saarejärve | 332 | 27 | 0.1 | 2.0 | Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) | 226 | G3.1 | 10 |

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|---|---|---|---|---|---|---|---|---|---|
| FI01 | Valkea-Kotinen | 30 | 4 | 0.25 | 1.3 | Norway spruce (*Picea abies*) | 18 | G3.A | 5 |
| | | | | | | Scots Pine (*Pinus sylvestris*) | 5 | G3.A | 5 |
| | | | | | | Norway spruce (*Picea abies*), Scots Pine (*Pinus sylvestris*), Birch (*Betula* spp.), Aspen (*Populus tremula*) | 4 | G4.2 | 5 |
| FI03 | Hietajärvi | 464 | 106 | 0.35 | 1.0 | Scots pine (*Pinus sylvestris*) | 198 | G3.A | 5 |
| | | | | | | Birch (*Betula* spp.), Scots Pine (*Pinus sylvestris*) | 15 | G4.2 | 5 |
| FI04 | Pesosjärvi | 636 | | - | - | Scots pine (*Pinus sylvestris*) | 493 | G3.A | 5 |
| | | | | | | Norway spruce (*Picea abies*), Birch (*Betula* spp.) | 31 | G4.2 | 5 |
| FI05 | Vuoskojärvi | 178 | - | - | - | Mountain birch (*Betula pubescens* ssp *tortuosa*) | 106 | G1.9 | 5 |
| | | | | | | Scots pine (*Pinus sylvestris*), mountain birch (*Betula pubescens* ssp *tortuosa*) | 24 | G3.A | 5 |
| GB01 | Allt'a Mharcaidh | 998 | 0 | 0 | 1.5 [b] | Bog | 200 | D1 | 5 [c] |
| | | | | | | Moss/lichen mountain summits | 200 | E4.2 | 5 [c] |
| | | | | | | Sub-arctic heath/moor | 499 | F2 | 5 [c] |
| | | | | | | Unmanaged conifers (pine) | 100 | G3.4 | 5 [c] |
| GB02 | Afon Hafren | 358 | - | - | - | Acid grassland | 107 | E1.7 | 10 [c] |
| | | | | | | Dwarf shrub heath | 107 | F4.11 | 10 [c] |
| ISO1 | Litla-Skard | 56 | - | - | - | Level mire | 3 | D2 | 10 |
| | | | | | | Sloping mires | 13 | D4 | 15 |
| | | | | | | Grassland | 4 | E4 | 5 |
| | | | | | | Mossheath (*Racomitrium* spp.) | 10 | F2 | 5 |
| | | | | | | Birch (*Betula pubescens*) | 15 | G1 | 10 |
| IT01 | Renon-Ritten | 0.3 | - | - | - | Spruce (*Picea abies*) | 0.2 | G3.1 | 10 |
| IT02 | Monticolo-Montiggl | 1.0 | - | - | - | Oak (*Quercus*) | 1 | G1.8 | 10 |
| IT03 | Passo Lavaze | 0.5 | - | - | - | Spruce (*Picea abies*) | 1 | G3.1 | 10 |
| IT05 | Selva Piana | 0.5 | - | - | - | Beech (*Fagus sylvatica*) | 1 | G1.6 | 10 |
| IT06 | Piano Limina | 0.5 | - | - | - | Beech (*Fagus sylvatica*) | 1 | G1.6 | 10 |
| IT07 | Carrega | 0.5 | - | - | - | Oak (*Quercus petraea*) | 1 | G1.8 | 10 |
| IT08 | Brasimone | 0.5 | - | - | - | Beech (*Fagus sylvatica*) | 1 | G1.6 | 10 |
| IT08 | Monte Rufeno | 0.5 | - | - | - | Oak (*Quercus cerris*) | 1 | G1.8 | 10 |

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|---|---|---|---|---|---|---|---|---|---|
| IT10 | Val Masino | 0.5 | - | - | - | Spruce (*Picea abies*) | 1 | G3.1 | 10 |
| IT11 | Roti | 0.5 | - | - | - | Oak (*Quercus cerris*) | 1 | G1.8 | 10 |
| IT12 | Colognole | 0.5 | - | - | - | Oak (*Quercus ilex*) | 1 | G2.1 | 10 |
| IT13 | La Thuile | 0.5 | - | - | - | Spruce (*Picea abies*) | 1 | G3.1 | 10 |
| LT01 | Aukstaitija | 102 | 0 | 0 | 3.9 | Birch (*Betula*) | 1 | G1 | 10 |
| | | | | | | Birch (*Betula*) and spruce (*Picea*) | 8 | G4 | 10 |
| | | | | | | Pine (*Pinus sylvestris*) | 35 | G3 | 5 |
| | | | | | | Spruce (*Picea*) | 45 | G3 | 5 |
| | | | | | | Spruce (*Picea*)-pine (*Pinus sylvestris*) | 13 | G3 | 5 |
| LT03 | Zemaitija | 147 | 0 | 0 | 2.0 | Birch (*Betula*) | 4 | G1 | 10 |
| | | | | | | Black alder (*Alnus glutinosa*) | 0.3 | G1 | 10 |
| | | | | | | Pine (*Pinus sylvestris*) | 4 | G3 | 5 |
| | | | | | | Spruce (*Picea*) | 60 | G3 | 5 |
| | | | | | | Spruce (*Picea*) and-pine (*Pinus sylvestris*) | 75 | G3 | 5 |
| LV01 | Rucava | 665 | 7 | 0.2 | 1.7 | Birch (*Betula pendula*) | 239 | G1 | 10 |
| | | | | | | Norway spruce (*Picea abies*) | 93 | G3 | 5 |
| | | | | | | Pine (*Pinus sylvestris*) | 326 | G3 | 5 |
| LV02 | Zoseni (Taurene) | 27 | 1 | 0.3 | 1.5 | Birch (*Betula*) | 2 | G1 | 10 |
| | | | | | | Norway spruce (*Picea abies*) | 8 | G3 | 5 |
| | | | | | | Pine (*Pinus sylvestris*) | 16 | G3 | 5 |
| NO01 | Birkenes | 42 | 0 | 0 | 0.5 | Aspen (*Populus tremula*) | 2 | G1 | 10 |
| | | | | | | Birch (*Betula*) | 2 | G1 | 10 |
| | | | | | | Norway spruce (*Picea abies*) | 33 | G3.A | 5 |
| | | | | | | Pedunculate oak (*Quercus robur*) | 1 | G1 | 10 |
| | | | | | | Rowan (*Sorbus*) | 0.2 | G1 | 10 |
| | | | | | | Scots pine (*Pinus sylvestris*) | 5 | G3.B | 5 |
| NO02 | Kårvatn | 2 500 | 100 | 0 | 0.3 | Scots pine (*Pinus sylvestris*) and alpine birch (*Betula nana*) | 450 | G4.2 | 5 |
| SE04 | Gårdsjön F1 | 4 | 0 | 0 | 0.8 | Birch (*Betula*) | 1 | G1 | 10 |
| | | | | | | Norway spruce (*Picea abies*) | 3 | G3.1 | 10 |
| | | | | | | Pine (*Pinus sylvestris*) | 1 | G3.1 | 10 |
| SE14 | Aneboda | 20 | 0 | 0.03 | 0.8 | Mixed norway spruce (*Picea abies*) and - scots pine (*Pinus sylvestris*) | 20 | G3.1 | 10 |

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|---|---|---|---|---|---|---|---|---|---|
| SE15 | Kindla | 19 | 0 | 0.03 | 0.8 | Norway spruce (*Picea abies*) | 19 | G3.A | 5 |
| SE16 | Gammtratten | 43 | 0 | 0.06 | 0.8 | Norway spruce (*Picea abies*) and pine (*Pinus sylvestris*) | 43 | G3.A | 5 |

[a] Area of lake, $f_{peat}$ and $N_{acc}$ given only for catchments used in mass balance critical loads analysis, for the other sites these variables are marked with '-' .

[b] This parameter is not used in the UK for mapping critical loads, as mass balance critical loads are calculated only for managed woodlands in the UK. For all other habitats, only empirical critical loads are used.

[c] The values used for mapping critical loads in the UK vary and are based on evidence of impacts (Hall et al. 2011).