Long-term sulphate and inorganic nitrogen mass balance budgets in European ICP Integrated Monitoring catchments (1990–2012)


Abstract

Empirical evidence based on integrated environmental monitoring including physical, chemical and biological variables is essential for evaluating the ecosystem benefits of costly emission reduction policies. The international multidisciplinary ICP IM (International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems) programme studies the integrated effects of air pollution and climate change on ecosystems in unmanaged and calibrated forested catchments. We calculated site-specific annual input-output budgets for sulphate (SO₄) and total inorganic nitrogen (TIN=NO₃⁻-N+N+NH₄-N) for 17 European ICP IM sites in 1990–2012. Temporal trends for input (deposition) and output (runoff water) fluxes and the net retention/net release of SO₄ and TIN were also analysed. Large differences in the input and output fluxes of SO₄ and TIN reflect important gradients of air pollution effects in Europe, with the highest deposition and runoff water fluxes at IM sites located in southern Scandinavia and in parts of Central and Eastern Europe and the lowest fluxes at more remote sites in northern European regions. A significant decrease in the total (wet + dry) deposition of non-marine SO₄ and bulk deposition of TIN was found at 90% and 65% of the sites, respectively. Output fluxes of non-marine SO₄ in runoff decreased significantly at 65% of the sites, indicating positive effects of the international emission abatement actions in Europe during the last 20 years. Catchments retained SO₄ in the early and mid-1990s, but this shifted towards a net release in the late 1990s, which may be due to the mobilization of legacy S pools accumulated during times of high atmospheric SO₄ deposition. Despite decreased deposition, TIN output fluxes and retention rates showed a mixed response with both decreasing (9 sites) and increasing (8 sites) trend slopes, and trends were rarely significant. In general, TIN was strongly retained in the catchments not affected by natural disturbances. The long-term annual variation in net releases for SO₄ was explained by variations in runoff and SO₄ concentrations in deposition, while a variation in TIN concentrations in runoff was mostly associated with a variation of the TIN retention rate in catchments. The net release of SO₄ from forest soils may delay the recovery from acidification for surface waters and the continued enrichment of nitrogen in catchment soils poses a threat to terrestrial biodiversity and may ultimately lead to a higher TIN runoff through N-saturation. Continued monitoring and further evaluations of mass balance budgets are thus needed.

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1. Introduction

Due to the extensive emissions of sulphur dioxide (SO₂) and nitrogen compounds (NOₓ, NH₃), acidification of sensitive ecosystems due to deposited acidifying compounds has received considerable attention as an international environmental problem in Europe and North America (e.g. Leivestad and Muniz 1976; Rodhe et al., 1995; Schindler, 1988; Ulrich et al., 1980; Wright et al., 2005). A sustained accumulation of deposited inorganic N also poses a threat to ecosystems through nutrient enrichment and nutrient imbalance (Bergström et al., 2005; Bergström and Jansson, 2006; Lepori and Keck, 2012; Stevens et al., 2011). It also poses a threat to biodiversity, as a consequence of the eutrophication of sensitive ecosystems, shown by the results of the international networks of forested sites from both ICP IM (International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems) and ICP Forests (International Cooperative Programme on Assessment and Monitoring of Air Pollution Effects on Forests) sites under UNECE CLRTAP (Dirmböck et al., 2014) and other studies (Bleeker et al., 2011; Bobbink et al., 2010; MEA, 2005; Sala et al., 2000). Deposition-induced N enrichment in forest soil may also deteriorate tree mineral nutrition (Jonard et al., 2014). In addition to airborne deposition, there is growing evidence that climate change causes impacts on the chemistry and ecology of freshwater ecosystems (e.g. Adrian et al., 2009; Shimoda et al., 2011). Many of the retention and release processes for sulphate and inorganic nitrogen are sensitive to climatic variables, and would, therefore, be affected by climate change (e.g. Dirmböck et al., 2016; Mitchell et al., 2013; Moore et al., 2010; Templar et al., 2012; Wright and Jenkins, 2001).

Observed detrimental effects of transboundary air pollution led to international negotiations on emission reductions under the Convention on Long-Range Transboundary Air Pollution (CLRTAP), signed in 1979 under the United Nations Economic Commission for Europe (UNECE, 1996). Since the 1980s, environmental regulations have led to declining emissions of air pollutants in Europe and North America. In Europe, overall emissions of SO₂ declined by 71% between the years 1990 and 2011 and those of nitrogen compounds by 42% (NOₓ) and 31% (NH₃), resulting in a declining deposition of air pollutants (Schulz et al., 2013). As indicated, the emission reduction measures have been less successful for nitrogen, compared to sulphur, and nitrogen emissions have stabilized (NOₓ) or increased slightly (NH₃) during the 2000s (Amann et al., 2013), and the decrease in inorganic nitrogen deposition has not been observed as strongly as for SO₂ (e.g. Waldner et al., 2014).

Following the drastic decrease in SO₂ deposition and SO₂ concentrations in surface waters, widespread recovery from the acidification of sensitive freshwater ecosystems has taken place in Europe and North America (Forsius et al., 2001; Garmo et al., 2014; Helliwell et al., 2014; Skjelkvåle et al., 2005; Stoddard et al., 1999; Wright et al., 2005). Accompanying a decreasing SO₂ deposition, forested catchments in Europe and North America have also shown a net release (output > input) of SO₄ from internal soil S sources. This process may be considered as a time-lagged recovery of terrestrial systems fuelled by the mobilization of legacy S pools accumulated during times of a high atmospheric SO₂ deposition (Augustaitis et al., 2010b; De Vries et al., 2003, 2001; Forsius et al., 2005; Löfgren et al., 2001; Mitchell et al., 2013, 2011; Prechtl et al., 2001; Watmough et al., 2005).

In the absence of significant N deposition, nitrogen is generally the growth-limiting nutrient in many forest ecosystems, so that the biological uptake of available nitrogen compounds through plants and soil microbes is efficient (Tamm, 1991). Undisturbed forest ecosystems receiving low to moderate inorganic N deposition retain most of the nitrogen in the catchments; typically < 10% is leached in runoff, mostly as NO₃ (e.g. Hedin et al., 1995; Wright et al., 2005). However, ecosystem nitrogen dynamics are inherently complex with biological processes, long-term response lags and high spatial and seasonal fluctuations (Aber et al., 2003; Augustaitis et al., 2010a; Bernal et al., 2012; Butterbach-Bahl et al., 2011; Lovett and Goodale, 2011). Sustained high inorganic N deposition may cause N-saturation of terrestrial ecosystems (N input and available inorganic N exceeds biotic demand) and excess NO₃ leaching to surface waters (Aber et al., 1989; Curtis et al., 2005; Dise and Wright, 1995; MacDonald et al., 2002; Oulehle et al., 2012) or increased losses of greenhouse gases (Kreutzer et al., 2009). However, excess NO₃ leaching through N-saturation may not be indicative at all sites (Lovett and Goodale, 2011). Although an elevated NO₃ loss from catchments can be associated with a high N deposition, e.g. as shown at IM sites by Holmberg et al. (2013), and has reached elevated levels in forested areas which are prone to chronic N deposition (Corre et al., 2007; Kiese et al., 2011; Thimonier et al., 2010), time trends in NO₃ concentrations in surface waters do not show a regionally consistent pattern (Garmo et al., 2014; Helliwell et al., 2014; Lovett and Goodale, 2011; Watmough et al., 2005; Wright et al., 2001). In addition to concerns related to eutrophication, the relative importance of oxidized and reduced N-compounds as acidifying agents is increasing, as nitrogen emissions have decreased much less than sulphur emissions (Helliwell et al., 2014).

In order to improve our ability to anticipate potential trends and support mass balance models (e.g. Hettelingh et al., 2007; Sverdrup and De Vries 1994) for the future surface water quality and SO₄ and inorganic N status of catchments in response to emission reductions, insights from long-term input-output budgets are useful. These budgets provide integrated, quantified responses to changes in deposition and allow the testing of hypotheses e.g. for changes in budget discrepancies of S and N in catchments with regard to other drivers, in particular climate. Previous mass balance budgets for SO₄ and inorganic N in ICP IM catchments in Europe were calculated as the average of three years (mainly 1997–1999) (Forsius et al., 2005). Thus, an extensive assessment of long-term changes in input-output budgets for S and N in IM catchments is lacking and, to our knowledge, little information on temporal changes in S and N mass balance budgets during the past 20 years in other forested catchments in Europe is available. In this paper, we calculate site-specific annual mass balance (input-output) budgets for sulphate (SO₄) and total inorganic nitrogen (TIN=NO₃-N+NH₄-N) and quantify the annual net retention or net release rates of SO₄ and TIN in the catchment, using available long-term data (longest time series in 1990–2012) collected in the international ICP IM network of forested research catchments in Europe. The main aims of the present study are: (i) to evaluate if deposition (input) and runoff (output) fluxes, and the retention and release rates of SO₄ and TIN have changed in the course of successful emission reductions in different regions in Europe; (ii) to assess if rates of changes in retention and release can be related to deposition levels and/or hydrology and/or catchment disturbance; and (iii) to assess the changes in fluxes and retention/release in the context of emission and deposition response reductions.

2. Materials and methods

2.1. Description of catchments

The long-term data used in this study rely on the monitoring of unmanaged and calibrated forest catchments belonging to the ICP IM network. The IM catchments are located in nature conservation areas or semi-natural areas with minimum direct human disturbance and have been relatively intact for even over 100 years, and are therefore suitable for the monitoring of air pollution effects on ecosystems (Manual for Integrated Monitoring, 1998). On the basis of the availability of internationally reported data in the ICP
Table 1
Basic catchment characteristics in studied IM catchments.

<table>
<thead>
<tr>
<th>Site code</th>
<th>Site name</th>
<th>Country</th>
<th>Catchment area (km²)</th>
<th>Altitude (m)</th>
<th>Forest area (%)</th>
<th>Lakes (%)</th>
<th>Peatland (%)</th>
<th>Predominant vegetation</th>
<th>Dominant bedrocks</th>
<th>Soil type</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT01</td>
<td>Zöbelboden</td>
<td>Austria</td>
<td>0.90</td>
<td>550–950</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>Norway spruce, European beech</td>
<td>Calcitic dolomite</td>
<td>Chromic Cambisols, Hydromorphic Stagnosols, Lithic and Rendzic Leptosols</td>
</tr>
<tr>
<td>CZ01</td>
<td>Anenske Povodi</td>
<td>Czechia</td>
<td>0.29</td>
<td>487–543</td>
<td>90</td>
<td>0</td>
<td>0</td>
<td>Norway spruce</td>
<td>Biotitic and sillimanitic-biotitic paragneiss</td>
<td>Dystric Cambisols</td>
</tr>
<tr>
<td>CZ02</td>
<td>Lysina</td>
<td>Czechia</td>
<td>0.27</td>
<td>829–949</td>
<td>100</td>
<td>0</td>
<td>6</td>
<td>Norway spruce</td>
<td>Leucogranite</td>
<td>Podzol, Gleysol</td>
</tr>
<tr>
<td>DE01</td>
<td>Forellenbach</td>
<td>Germany</td>
<td>0.69</td>
<td>787–1293</td>
<td>95</td>
<td>0</td>
<td>30</td>
<td>Norway spruce, European beech</td>
<td>Granite, gneiss</td>
<td>Dystric and Podzolic Cambisols, Rankers and Lithosols</td>
</tr>
<tr>
<td>EE02</td>
<td>Saarejärve</td>
<td>Estonia</td>
<td>3.32</td>
<td>44–77</td>
<td>68</td>
<td>8</td>
<td>10</td>
<td>Norway spruce, Scots pine</td>
<td>Sandstone, limestone</td>
<td>Podzols</td>
</tr>
<tr>
<td>FI01</td>
<td>Valkea-Kotinen</td>
<td>Finland</td>
<td>0.30</td>
<td>150–190</td>
<td>86</td>
<td>13</td>
<td>19</td>
<td>Norway spruce, Scots pine</td>
<td>Mica gneiss</td>
<td>Dystric Cambisols, Histosols</td>
</tr>
<tr>
<td>FI03</td>
<td>Hietajärvi</td>
<td>Finland</td>
<td>4.64</td>
<td>165–214</td>
<td>55</td>
<td>23</td>
<td>35</td>
<td>Scots pine dominated</td>
<td>Porphyritic granodiorites</td>
<td>Podzols</td>
</tr>
<tr>
<td>LT01</td>
<td>Aukstaitija</td>
<td>Lithuania</td>
<td>1.02</td>
<td>159–189</td>
<td>100</td>
<td>0</td>
<td>10</td>
<td>Norway spruce, Scots pine</td>
<td>Sandstone, limestone</td>
<td>Podzols</td>
</tr>
<tr>
<td>LT03</td>
<td>Zemaitija</td>
<td>Lithuania</td>
<td>1.47</td>
<td>147–180</td>
<td>100</td>
<td>0</td>
<td>20</td>
<td>Norway spruce, Scots pine</td>
<td>Sandstone, limestone</td>
<td>Podzols</td>
</tr>
<tr>
<td>LV01</td>
<td>Rucava</td>
<td>Latvia</td>
<td>6.65</td>
<td>6–16</td>
<td>99</td>
<td>1</td>
<td>18</td>
<td>Scots pine, birch, Norway spruce</td>
<td>Sandstone, limestone</td>
<td>Haplic Podzol on sand parental soil</td>
</tr>
<tr>
<td>LV02</td>
<td>Zoseni</td>
<td>Latvia</td>
<td>0.27</td>
<td>184–192</td>
<td>100</td>
<td>0</td>
<td>30</td>
<td>Scots pine, Norway spruce</td>
<td>Sandstone, limestone</td>
<td>Haplic Podzol on sand parental soil</td>
</tr>
<tr>
<td>NO01</td>
<td>Birkenes</td>
<td>Norway</td>
<td>0.41</td>
<td>200–300</td>
<td>90</td>
<td>0</td>
<td>7</td>
<td>Norway spruce, Scots pine</td>
<td>Granite</td>
<td>Podzols, Histosols, Leptosols</td>
</tr>
<tr>
<td>NO02</td>
<td>Kårvatn</td>
<td>Norway</td>
<td>25</td>
<td>200–1375</td>
<td>18</td>
<td>4</td>
<td>2</td>
<td>Scots pine, alpine birch</td>
<td>Gneiss, quartzite</td>
<td>Podzols</td>
</tr>
<tr>
<td>SE04</td>
<td>Gårdsjön</td>
<td>Sweden</td>
<td>0.04</td>
<td>114–140</td>
<td>95</td>
<td>0</td>
<td>10</td>
<td>Norway spruce</td>
<td>Granite</td>
<td>Podzol, Gleysol</td>
</tr>
<tr>
<td>SE14</td>
<td>Aneboda</td>
<td>Sweden</td>
<td>0.19</td>
<td>210–240</td>
<td>99</td>
<td>0</td>
<td>17</td>
<td>Norway spruce, Scots pine</td>
<td>Granite</td>
<td>Podzol, Histosols, Histosols</td>
</tr>
<tr>
<td>SE15</td>
<td>Kindla</td>
<td>Sweden</td>
<td>0.20</td>
<td>312–415</td>
<td>99</td>
<td>0</td>
<td>24</td>
<td>Norway spruce</td>
<td>Granite</td>
<td>Podzol, Histosols</td>
</tr>
<tr>
<td>SE16</td>
<td>Gammuntratten</td>
<td>Sweden</td>
<td>0.45</td>
<td>410–545</td>
<td>99</td>
<td>0</td>
<td>16</td>
<td>Norway spruce, Scots pine</td>
<td>Granite</td>
<td>Podzol, Histosols</td>
</tr>
</tbody>
</table>
IM database, we used 17 catchments which had a complete data set for annual mass balance calculations, covering deposition (both bulk and throughfall deposition) and runoff water chemistry and runoff volume (Fig. 1; Table 1).

The multidisciplinary ICP IM under the CLRTAP has been conducted since the late 1980s, enabling a cause-effect approach to study the long-term effects of air pollution and climate change on ecosystems in forested catchments across Europe with different deposition, climate and acidification and eutrophication potential. The ICP IM network provides the only data set that uses consistent and simultaneous physical, chemical and biological measurements over time from atmosphere and terrestrial and aquatic ecosystems across Europe. Many of the sites also belong to the LTER-Europe network for long-term ecosystem research.

The dominant vegetation in the monitored catchments mainly consists of northern and central European coniferous and broadleaf forests (Table 1). The type of bedrock and soil within the catchment areas varies widely; some consist of sorted sediments on sedimentary bedrock, others are till soils on igneous bedrock and some sites contain extensive peatlands and lakes. Mineral soils dominate most of the catchments, but some of the catchments include considerable areas of peaty soils.

The soils in Fennoscandia (Finland, Sweden and Norway) within northern Europe are thin and young glacial or supra-aquatic acid-sensitive soils with underlying granite bedrock. The sites in the Baltic States are located in areas with thick surface deposits and sandstone and limestone present. The soils in the Czech site CZ02 are thin unglaciated soils with acid-sensitive granite bedrock, while soils in another Czech site CZ01 are medium-deep to deep unglaciated soils with underlying acidic paragneiss bedrock. The soils in the German site (DE01) are thin to medium-deep soils, glaciated in summit regions and upper parts of the slopes with
underlying acid-sensitive granite bedrock. Karstic conditions exist in the Austrian site (AT01), with dolomite bedrock.

2.2. Calculation of ion fluxes

2.2.1. Input (deposition) fluxes

Methods for the collection, storage and analysis of bulk deposition and throughfall samples are described in the programme manual (Manual for Integrated Monitoring, 1998). Bulk deposition samples, including the precipitation amount and chemistry of bulk precipitation, were collected on open locations within or adjacent to each catchment, using HDPE (high-density polyethylene) plastic funnel collectors. At some sites, the precipitation amount for the deposition estimate was obtained from meteorological rain gauges situated within the catchment or from the closest climate station nearby. At sites with regular winter conditions (snow cover), cylindrical HDPE collectors or purpose-made plastic bags were used to collect the winter snowfall. Throughfall samples (wash-off of dry deposition and leachates produced by the canopy to the forest floor) were collected separately under the canopy, using 10–20 funnel shaped collectors, which were placed randomly or systematically around the plot or in a grid. During winter, at the sites with snow cover, snow collectors (plastic ring and attached plastic bag) were used to collect snowfall under the canopy. Generally, the deposition samples were collected on a weekly basis in the field, stored at 4 °C and analysed as a monthly composite sample. A monthly precipitation sum has been used at all sites to calculate the deposition.

As IM sites are almost totally forested catchments, dry deposition (gases and particles filtered by the canopy) highly contributes to the total deposition. The total deposition of SO4 to the catchment including wet and dry deposition fractions was estimated from the bulk deposition and throughfall measurements by calculating the annual deposition, both to the defined open area (bulk) and the forest area (throughfall), and then summing up the area-weighted open area and throughfall deposition (see Forsius et al., 2005). Because of a strong canopy interaction for reduced N (NH₄) and oxidized N (NO₃), as shown by the difference between open area (bulk) and throughfall NH₄ and NO₃ deposition measurements (see Table 2), bulk deposition measurements were used for the total deposition of inorganic nitrogen (see Forsius et al., 2005). At a majority of IM sites (15 out of the 17 sites), the long-term average (1990–2012) for the bulk deposition of TIN was higher than that of throughfall, due to an inorganic N uptake by plant tissue and through stomata (Draaijers and Erisman, 1995). This approach may overestimate or underestimate the real total TIN deposition to the forest floor, depending on e.g. the magnitude of N uptake by foliage or the amount of dry deposition in an open area. In addition to these factors, other canopy interactions, such as TIN immobilization in the canopy (e.g. Ferm, 1993; Garten et al., 1998) and the impaction (horizontal deposition or direct absorption of gases, such as HNO₃ vapour) (e.g. Chapin et al., 2011) may cause uncertainties in the estimated total TIN deposition. Monthly deposition fluxes were calculated as the product of the respective ion concentrations with monthly precipitation sums. Annual deposition fluxes were calculated by summing up monthly fluxes, and are expressed as meq m⁻² yr⁻¹.

2.2.2. Output (runoff) fluxes

Runoff water chemistry sampling was carried out, usually weekly or fortnightly, in the catchment outlet streams at weirs, with continuous recording of the water level-based runoff. At some sites, runoff water chemistry samples were collected monthly during the base-flow period in winter and summer. As the quantitative calculation of the runoff at the site AT01 is impeded by the karstified geology, runoff at the weir and the extended catchment was modelled by a process-based semi-distributed karst model (Hartmann et al., 1993; J. Vuorenmaa et al., 1996).
et al., 2016, 2012). Using data reported to the IM database, output fluxes from the catchments were calculated as the product of measured catchment runoff and ion concentrations. Annual output fluxes of SO$_4$ and TIN were calculated by summing monthly fluxes, obtained from monthly runoff and flow-weighted monthly mean solute concentration, and are expressed as meq m$^{-2}$ yr$^{-1}$. The methods for the collection, storage and analysis of runoff water chemistry samples are described in the programme manual (Manual for Integrated Monitoring, 1998).

2.2.3. Catchment retention

In order to quantify the net retention or net release of SO$_4$ and TIN in the catchment, a percent net export (pne) was calculated. The percent net export (%) is defined as: pne = (output – deposition) * 100 / deposition. The negative pne value indicates the net retention and the positive pne value indicates the net release in the catchment.

2.2.4. Statistical analysis

The dependence between deposition, output and water fluxes and retention/release rates was analysed by using correlation and stepwise multiple regression techniques. Correlation matrices to examine relationships between precipitation, runoff water volume, output fluxes and deposition and percent net export (pne) of SO$_4$ and TIN in the entire dataset were calculated by using non-parametric Kendall’s tau-b test (e.g. Conover, 1980). Kendall’s rank correlation test is not sensitive to outliers and the non-linear relationship between variables, and does not require the assumption of normality. Kendall’s tau-b correlation coefficients ($\tau_b$) were calculated by using the annual mean values for the entire dataset during the period 1990–2012. A statistical significance threshold of p < 0.05 was applied to the significance of the correlation. Stepwise multiple regression analysis was applied for each of the study sites to explain the annual variation in pne of SO$_4$ and TIN in 1990–2012. The explaining variables were precipitation to the forest floor, runoff water volume, volume-weighted concentrations of SO$_4$ in the total deposition and TIN in the bulk deposition and volume-weighted concentrations of SO$_4$ and TIN in runoff water. Precipitation to the forest floor was calculated by using area-weighted open area and throughfall precipitation values. Stepwise regression analysis used forward and backward selection, and only explaining variables having a significance of p < 0.05 were included in the model. Statistical analyses were performed by using SAS Enterprise Guide version 5.1 for Windows.

For detecting long-term monotonic trends in mass balance compartments and hydrometeorological variables for each of the study sites, the non-parametric Mann-Kendall test (MKT) (Hirsch et al., 1982) was applied to annual data. MKT is not particularly sensitive to missing data and outliers, and requires no assumption of normality. A Visual Basic program for a multivariate and conditional Mann-Kendall test of monotonic trends (available at www.slu.se/PageFiles/62531/Mann-Kendall_Sen.xls) was used for the trend detection (Libiseller and Grimvall, 2002). The magnitude of trend slope was estimated by the Theil-Sen slope estimation method (Sen, 1968), and is expressed as meq m$^{-2}$ yr$^{-1}$ for fluxes, % yr$^{-1}$ for pne values and mm yr$^{-1}$ for precipitation and runoff. A statistical significance threshold of p < 0.05 was applied to the trend analysis. A p value of < 0.1 was used to indicate a weak and not statistically significant trend, which can, however, be considered to show an increasing/decreasing tendency in the record.

To distinguish changes in anthropogenic SO$_4$ from climate-related variations in sea-salt, trends for deposition and output fluxes were calculated, using non-marine fraction of SO$_4$. The sea-salt corrected fraction was calculated by subtracting the marine contribution estimated from the ratio of the ion to Cl in seawater (Lyman and Fleming, 1940), and is hereafter denoted as xSO$_4$.

The sites DE01, SE14 and EE02 were excluded from the aggregate data analysis of TIN. Elevated concentrations and fluxes of TIN at the site EE02 are partly due to inputs of N fertilizers from crop agriculture (Holmberg et al., 2013), and at sites DE01 and SE14 due to substantially altered biogeochemical N cycles within the catchments by well-known forest disturbance regimes (i.e. wind-throw, bark beetle infestation) (Beudert et al., 2014; Lüggen et al., 2013). Therefore, they were not considered to be representative of the effect of N deposition.

3. Results

3.1. Gradients and trends in deposition fluxes of SO$_4$ and TIN

The studied IM areas exhibit a great range of hydrological conditions. The highest annual mean precipitation (>1000 mm yr$^{-1}$) occurred in coast-near stations in the vicinity of the North Atlantic Ocean in Norway (NO01, NO02) and in the south-western part of Sweden (SE04), and in high altitude regions in Central Europe (AT01, CZ02 and DE01) (Table 2). The other Swedish IM sites SE14, SE15 and SE16 are intermediary, while the Czech site CZ01 and the sites in Finland and the Baltic States are located in lowland areas and have relatively low annual precipitation. The annual precipitation amount showed only a few significant trends with a significant increase at two sites (CZ01, LV02) (Table 3). Other sites showed predominantly positive trend slopes in precipitation, but these were not significant.

The deposition of SO$_4$ and TIN showed large differences between the sites, with the highest values at sites located in parts of Central and Eastern Europe and the lowest values at sites in northern regions. The sites in southern Fennoscandia (NO01, SE04) were also exposed to high SO$_4$ and TIN depositions (Fig. 2, Table 2). The total deposition of SO$_4$ was higher than the bulk deposition of SO$_4$ at many study sites, indicating the importance of dry deposition fraction for total deposition.

The study sites that have been exposed to the highest total SO$_4$ deposition in the 1990s (>100 meq m$^{-2}$ yr$^{-1}$) showed the strongest reductions in the deposition (Fig. 2; Table 3). At these sites, SO$_4$ deposition has substantially decreased from a level of 150–250 meq m$^{-2}$ yr$^{-1}$ to <50 meq m$^{-2}$ yr$^{-1}$ during the period 1990–2012. The total (i.e. wet + dry) deposition of non-marine SO$_4$ (i.e. anthropogenic SO$_4$ deposition, xSO$_4$) exhibited a significant downward trend at all study sites within the study period. The low deposition site SE16 showed a decreasing tendency in trend in the bulk deposition (i.e. largely wet) of xSO$_4$ (−0.46 meq m$^{-2}$ yr$^{-1}$, p = 0.055). The total deposition of xSO$_4$ decreased from 1990 through 2012, more than the bulk deposition of xSO$_4$ (Table 3).

The bulk deposition of TIN decreased at 16 out of the 17 sites during 1990–2012, and a downward trend was significant at 11 (65%) of the sites. Correspondingly, the throughfall deposition of TIN decreased at 13 out of the 17 sites with a significant decrease at seven of the sites. On average, the decrease of TIN in bulk deposition was steeper than the decrease of TIN in throughfall during 1990–2012 (Table 3).

3.2. Gradients and trends in runoff water fluxes of SO$_4$ and TIN

Similar to the precipitation pattern, the highest runoff occurred at sites located in south-western Scandinavia and in central parts of Europe and lowest values at the site CZ01 and sites in Finland and the Baltic States. The forest at DE01 consists of ca. 60% of young spruce and mixed stands regenerating from a bark beetle attack; at this site, annual runoff increased due to decreased evapotranspiration (Bernsteinová et al., 2015). Annual runoff showed both positive
Table 3
Temporal trends (1990–2012) for annual climatic variables and mass balance compartments of SO4 and TIN in studied IM catchments (P = precipitation, RW = runoff water volume, BD = bulk deposition, TD = total deposition, TF = throughfall deposition, output = runoff water flux, ppe = percent net export, n.d. = no data). Input and output fluxes for SO4 are presented as non-marine fractions (denoted as xSO4). For the annual change, a significant trend (p < 0.05, Mann-Kendall test, Sen's slope) is in bold. Site-specific annual changes and their mean and median (Md.) values for climatic variables, deposition and output fluxes and ppe values are given in mm yr⁻¹, meq m⁻² yr⁻¹ and % yr⁻¹, respectively.

<table>
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<th>TIN BD</th>
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Fig. 2. The annual total deposition of SO4 (meq m⁻² yr⁻¹) in IM catchments CZ01, CZ02, LT03, NO01 and SE04 (a) and the annual bulk deposition of inorganic N (TIN) (meq m⁻³ yr⁻¹) in IM catchments AT01, CZ02, DE01, NO01 and SE04 (b) in 1990–2012.

(10 sites) and negative (7 sites) trend slopes, but the trends were rarely significant (Table 3).

Similar to the deposition gradients, there were large differences in the annual output fluxes of SO4 in runoff between the different sites. The highest fluxes of SO4 were observed at IM sites located in parts of south-western Scandinavia, Central and Eastern Europe and the lowest fluxes at sites in parts of northern regions (Table 2). Annual output fluxes of xSO4 decreased at 15 out of 17 sites during 1990–2012, being significant at 11 (65%) of the sites. Output fluxes of xSO4 at the sites FI01 and SE16 located in the northern region have intermediate or low deposition/runoff fluxes, respectively, showed a decreasing tendency (-0.65 meq m⁻² yr⁻¹, p = 0.053 and -0.91 meq m⁻² yr⁻¹, p = 0.089, respectively). The mean output fluxes and deposition of SO4 showed a significant positive correlation (rB = 0.62, p < 0.001, Table S1, Supplementary material), thus indicating that a high leaching of SO4 was associated with a high deposition of SO4. On average, the fluxes of xSO4 in runoff have decreased less than in the total deposition (Table 3).

The highest annual output fluxes of TIN were found at sites located in parts of Central and Eastern Europe and decreasing gradually towards the northern region (Table 2). Time trends in output fluxes of TIN showed a mixed response with both decreasing (9 sites) and increasing (8 sites) trend slopes. It decreased significantly at five sites (CZ01, CZ02, FI03, LV02, SE15), while increasing significantly at two sites (DE01 and SE14) (Table 3). The output flux of NO3 also increased significantly at the site SE04. TIN flux in runoff showed an increasing tendency at the site AT01 (1.21 meq m⁻² yr⁻¹, p = 0.053). Like for SO4, the leaching of TIN increases with increasing TIN deposition (rB = 0.71, p < 0.001) (Table S2, Supplementary material).

3.3. Changes in catchment retention

3.3.1. Sulphate (SO4)

The mass balance budgets for SO4 showed a high year-to-year variation in percent net export (ppe) within catchments, as shown for example at CZ01 (Fig. 3a), DE01 (Fig. 3c), FI01 (Fig. 3e), SE04 (Fig. 3g) and NO01 (Fig. 3i). Despite that most of the catchments showed a change from retention towards increasing net release in the course of the study period (Table 3 and Table S3, Supplementary material). Increasing ppe i.e. declining retention/increasing net release of SO4 occurred in 13 out of 17 sites during 1990–2012, being significant at eight sites, and tending to increase at sites AT01 (0.88% yr⁻¹, p = 0.062) and FI01 (1.9% yr⁻¹, p = 0.076). The results from IM sites with the longest monitoring records since 1990/1991 (CZ01, CZ02, DE01, FI01, FI03, NO01, NO02, SE04) showed that catchments, in general, retained SO4 (input > output) in the early 1990s, but since the late 1990s, they commonly shifted towards a
Fig. 3. Annual runoff (mm yr⁻¹) (left and right column, bar) and percent net export (pne, % yr⁻¹) of SO₄ and inorganic N (TIN) (left and right column, solid and dashed line, respectively) for CZ01 (a, b), DE01 (c, d), FI01 (e, f), SE04 (g, h) and NO01 (i, j) in 1990–2012.
and SE04 in 1990–2012 (a and b, respectively) and AT01, CZ01, CZ02, DE01, EE02, FI01, FI03, LT01, LT03, LV01, LV02, NO01, NO02, SE04, SE14, SE15 and SE16 in 2000–2012 (c and d, respectively). The lower and upper lines indicate 25th and 75th percentiles, respectively, and a dot indicates the median value. DE01, EE02 and SE14 were omitted from the calculation of percentiles for TIN pme. The 75th percentile for SO4 pme (279%) in 2012 in Fig. 4a) is outside the axis range and not shown in the graph.

Net release (output > input). Combining the annual-based SO4 pme values for these eight sites, the annual median values exhibited a significant increase (SO4 pme 3.2% yr$^{-1}$, $p=0.0002$) in 1990 – 2012 (Fig. 4a). The corresponding record for all of the study sites in 2000 – 2012 also exhibited a significant upward trend (SO4 pme 4.2% yr$^{-1}$, $p=0.015$) (Fig. 4c).

Long-term changes of catchment net retention and release for SO4 can be observed, both in high and low SO4 deposition areas. The site CZ02 in Central Europe was exposed to high SO4 deposition (>200 meq m$^{-2}$ yr$^{-1}$) in the early 1990s, followed by a drastic decrease of SO4 deposition during the middle and late 1990s. SO4 output decreased as well, but less than input in the deposition, and since the late 1990s SO4 output increasingly exceeded input, which is indicated by an increase in SO4 pme (Fig. 5a). In the low SO4 deposition area (<30 meq m$^{-2}$ yr$^{-1}$) at the site FI03 in northern remote region, SO4 was mainly retained in the catchment, but the retention rate declined over the study period, and at the end of the study period, SO4 input roughly equaled output (Fig. 5c).

There was a significant negative correlation between the annual change of SO4 pme and the annual change of SO4 deposition ($r_B = -0.52$, $p=0.004$), and a marginal positive correlation between the annual change of SO4 pme and mean SO4 deposition load ($r_B = 0.34$, $p=0.058$) (Table S1, Supplementary material). This means that the recovery of forested catchments from SO4 deposition – in terms of SO4 net release – appeared to be most pronounced in catchments with the highest SO4 deposition level and also having the strongest decrease in the SO4 deposition load. In addition, there was a marginal positive relationship between the mean SO4 fluxes and mean pme values of SO4 ($r_B = 0.33$, $p=0.064$) suggesting that in general, the high pme value of SO4 was associated with the high SO4 output flux.

The long-term annual variation in SO4 pme values was mostly explained by variations in the runoff water volume and SO4 concentration in precipitation (Table S4, Supplementary material). The variation in runoff was the first predictor at eight sites (AT01, FI01, LT03, LV02, SE04, SE14, SE15, SE16), and the regression model gave partial R-squares for runoff – as a first predictor variable – from 0.20 to 0.68. The association between annual variation in runoff and SO4 pme values, however, emerges primarily since the late 1990s (Fig. 3a, c, e, g). The decreasing trend of SO4 concentrations in deposition was first predictor variable at six sites (CZ02, DE01, FI03, LT01, NO01, NO02), and the model gave partial R-squares for the deposition – as a first predictor variable – from 0.31 to 0.70. The long-term annual variation in SO4 concentrations in runoff was mostly associated with a variation in SO4 pme values only at two sites (CZ01, LV01).

### 3.3.2. Inorganic nitrogen (TIN)

The percent net export of TIN (TIN pme) generally varied between −98% and −80% in IM catchments during 1990–2012 (Figs. 4b and 4d). During the period 2005–2012, the retention of deposited TIN was >90% in most of the unmanaged catchments (Table S5, Supplementary material). These results show that the export of inorganic N in runoff was clearly less than the input through deposition. If sites DE01 and EE02 were excluded, between 38 and 100% of TIN input in the deposition was retained across the study catchments with a median value of 95%. In general, the mean TIN retention rate in the catchment declined with the increased mean deposition level ($r_B = 0.38$, $p=0.06$) and the mean output flux of TIN ($r_B = 0.67$, $p=0.0008$) (Table S2, Supplementary material).

Combining the annual median values of TIN pme for the sites CZ01, CZ02, FI01, FI03, SE04, NO01 and NO02, the annual median values exhibit a significant decrease ($-0.12$% yr$^{-1}$, $p=0.013$), i.e. the retention rate of deposited TIN increased during 1990–2012 (Fig. 4b). Regarding all studied catchments, however, site-specific trends in the annual retention rate of TIN showed a similar pattern to that detected in TIN output fluxes i.e. a mixed response with both decreasing and increasing trend slopes. The annual median TIN pme for all the sites in 2000 – 2012 did not exhibit any increasing or decreasing significant trend (Fig. 4d). A decreased retention
rate occurred at eight sites and an increased retention rate at nine sites. The retention rate of TIN significantly increased only at one site (CZ02), and an increasing tendency was detected at two sites: CZ01 (−0.15% yr⁻¹, p = 0.060) and SE16 (−0.15% yr⁻¹, p = 0.089). The retention rate declined significantly at sites LV01, SE04 and SE14, and the net release (output > input) of TIN increased significantly in DE01. A tendency towards a declining retention rate was observed at site LT03 (0.12% yr⁻¹, p = 0.089). An increased net release and decreased retention at sites DE01 and SE14, respectively, were due to a disrupted N cycle in those catchments. At site LV01, the TIN deposition decreased significantly and the catchment exhibited a strong retention ability (values of TIN pene between −91% and −86% in 2005−2009) (Table S5, Supplementary material), but the annual change in the output flux of NO₃ exhibited a relatively high (although not significant) increase (0.11 meq m⁻² yr⁻¹). This pattern was indicated by a decreased retention rate of TIN.

The long-term variation in TIN concentrations in runoff water was mostly associated with a variation in TIN pene values and a variation in concentrations was the first predictor variable in 12 IM catchments, while the variation in the runoff water volume was the dominant predictor variable at only three sites (CZ01, FI01 and EE02, see Fig. 3b and f and Table S4, Supplementary material).

4. Discussion

4.1. Changes in input-output budgets of SO₄

The large differences in SO₄ deposition reflects well-known emission and deposition gradients of air pollutants in Europe (Lövblad et al., 2004; Waldner et al., 2014). Central and Eastern Europe were historically large sources of emissions, and thus sites in the region (e.g. CZ01, CZ02, LT03, DE01, LV01, AT01) received the highest anthropogenic SO₄ deposition, while the long-range transport and deposition of SO₄ decrease gradually towards northern remote regions. The high SO₄ deposition at sites in southern Scandinavia (NO01, SE04) was due to the elevated long-range transport and can also be explained, at least partly, by high amounts of precipitation. For sites near the coast (e.g. NO01, NO02 and SE04), there is an important component of non-anthropogenic sea-salt SO₄ in the deposition (Table 2).

Successful emission reduction measures in Europe over the past 30 years have led to a declining deposition of air pollutants in countries (Schulz et al., 2013), as shown at IM sites. The emission control programmes have been most successful for sulphur, and the total deposition of xSO₄ decreased at studied IM sites located in the historically high S emission and deposition regions in Central-Eastern Europe by 70−80%, and in the northern remote regions by 40−70% between 1990 and 2012. The dry deposition of xSO₄ decreased more than the bulk (wet) deposition (ΔTotal deposition > Δ Bulk deposition), which is in agreement with previous studies for a number of European forested catchments (Prechtel et al., 2001; Waldner et al., 2014). SO₄ concentrations in throughfall are influenced by interception deposition, where the relative decrease has been even more pronounced, because improved emission control techniques and fuel-switching away from high sulphur-containing solid and liquid fuels to low sulphur fuels have markedly reduced S-containing gases and particles in emissions and ambient air concentrations in Europe (Aman et al., 2013).

The substantial decrease of xSO₄ deposition has evidently resulted in decreased output fluxes of xSO₄ in IM catchments. Although the annual runoff was increasing, rather than decreasing, our results for the period 1990−2012 showed that 65% of the sites exhibited a significant decrease in output fluxes. The previous trend assessment for the IM sites in 1993−2006 showed that xSO₄ output fluxes in catchments used in the present study decreased significantly at only 40% of the sites (Vuorenmaa et al., 2009). This suggests that IM catchments have increasingly responded to the decreases in the emission and deposition of SO₄ in Europe. At the same time, a much larger proportion of the sites (80%) showed statistically significant decreasing trends in xSO₄ concentrations (Vuorenmaa et al., 2009). Short-term inter-annual fluctuations in runoff volume, which largely modify the output fluxes of SO₄, can
therefore mask long-term changes in matter dynamics in ecosystems. Our results are consistent with the recent trend analysis of surface water chemistry in 173 acid-sensitive sites from 12 regions in Europe and North America as part of the UNECE ICP Waters programme (Garmo et al., 2014), and are in line with another recent European trend assessment of surface water SO4 concentrations (Hellrull et al., 2014), which both demonstrated clear decreases of SO4 concentrations in surface waters that eventually resulted from decreased SO4 loss into the watercourses.

The studied IM catchments vary in their sensitivity to acidification, and based on the surface water chemistry, the sites in Sweden and Norway and the Finnish site FI01 and Czech site CZ02 are considered to be susceptible to acidification (Acid Neutralizing Capacity: ANC < 100 μeq l−1) (Holmberg et al., 2013). The most acid-sensitive IM catchments in the present study with negligible/low buffering capacity are experiencing a recovery from sulphate-driven acidification, and increases in pH and ANC in the soil-water ecosystem that resulted from a decreased SO4 loss have been documented for CZ02 (Krám et al., 2012), FI01 (Ukonmaanaho et al., 2014; Vuorenmaa et al., 2014), NO01 (Wright, 2008) and Swedish sites SE04, SE14, SE15 and SE16 (Löfgren et al., 2011).

The trends in the net release of SO4 in IM catchments were generally increasing, and are consistent with previous surveys of element fluxes through the forest ecosystem in the late 1990s for a considerable number of the intensive monitoring forest plots (De Vries et al., 2003, 2001). Prechtl et al. (2001) demonstrated for 20 European forested catchments that most catchments started a net release of SO4 during the early 1990s. Mitchell et al. (2013, 2011) reported for 15 acid-sensitive catchments in North America that most of the catchments exhibited net releases of SO4 from 1984 through 2010. A survey of 21 catchments in 17 regions in Canada, the United States and Europe also demonstrated that in the majority of the sites (86%) SO4 export exceeded input, and the net release was greatest at sites that currently received the highest SO4 deposition (Watmough et al., 2005). An increasing net release of SO4 from internal sources in forest catchment soils is anticipated to indicate the recovery of these systems from previous episodes of a high atmospheric deposition of SO4. In the future, catchments are expected to approach to a “new” steady-state with respect to a contemporary lower SO4 deposition (De Vries et al., 2001; Mitchell et al., 2013). The properties of soils, such as the soil thickness, age, adsorption capacity and weathering, depending on the glaciated/unglaciated origin, may largely modify the size of soil S-pools and their dynamics. According to the Rice et al. (2014), the old unglaciated soils in the Southeastern United States may still considerably retain SO4, but should convert from retaining to releasing SO4 over the next two decades.

Our results show that the recovery of forested catchments from SO4 deposition – in terms of SO4 net release – is still ongoing in European forested catchments, and it has taken place in different types of catchments with a variety of soils and hydrological conditions, as well as different deposition levels and acidification potential. A long-term variation in amount of runoff in particular contributed to the net release of mobilized SO4 in IM catchments, but the role of runoff became increasingly important during the 2000s, in conditions of shifts from catchment retention towards net release. Watershed discharge may affect a number of chemical and biotic processes that can enhance SO4 mobilization from forest soils and hence leaching into watercourses. These processes would include increased S mineralization from the organic S pool of forested soils and desorption of SO4 (see Mitchell et al., 2013). It has previously been shown that climate-driven changes in hydrological conditions, such as increased watershed wetness and runoff and wetting and drying cycles, together with internal SO4 sources, are becoming increasingly important, as atmospheric SO4 input has declined (Benčóková et al., 2011; Dillon et al., 1997; Mitchell et al., 2013; Rice et al., 2014; Wright, 1998; Wright and Jenkins, 2001).

Our focus in this paper was on large-scale spatial and temporal patterns, and we did not analyse what specific processes in soils (the oxidation of reduced S species, S mineral weathering, desorption of previously adsorbed SO4, net organic S mineralization) were contributing to the discrepancy in input-output SO4 budgets. These latter two sources were anticipated to be the major sources of internal SO4 in the Adironack Mountains (New York, USA) that resulted from legacy deposits of atmospheric SO4 deposition (Mitchell et al., 2013). Prechtl et al. (2001) also suggested that desorption processes and the excess mineralization of organic S largely explained the net release of SO4 in response to decreased levels of deposition in many forest catchments in Europe. We would, therefore, assume that legacy deposits of atmospheric SO4 deposition are the main source of internal S in IM catchments and that it is likely that these two processes regulating a long-term increase in SO4 net release from soils are also strongly involved in IM catchments.

4.2. Changes in input-output budgets of inorganic nitrogen

The deposition levels of TIN at IM sites reflect gradients in emissions and long-range transboundary air pollution, similar to SO4. European nitrogen emissions have also decreased, which have resulted in a decrease of TIN deposition at a majority of IM areas, but a decrease of TIN deposition has been generally smaller than that of SO4 deposition. European emissions of nitrogen have decreased less than those of sulphur, and the bulk deposition of TIN has generally exceeded SO4 deposition on an equivalent basis since the late 1990s (Fig. 2; Forsius et al., 2005). Like for SO4, significant decreases of TIN in throughfall deposition at many of the IM sites may indicate the pronounced effect of declining dry deposition as well.

Enhanced TIN leaching from IM catchments was associated with high deposition inputs of TIN. An elevated N deposition has been found to be related to elevated inorganic N concentrations in soil water and inorganic N leaching in many areas in Europe (Gundersen, 1995; Iost et al., 2012; Waldner et al., 2015). Nitrate leaching mainly occurs when the inorganic N deposition input is above a critical deposition threshold of ca. 10 kg ha−1 yr−1 (Dise and Wright, 1995; Kaste et al., 2007; MacDonald et al., 2002; Stoddard et al., 2001; Wright et al., 2001). The mean annual bulk TIN deposition in the unmanaged IM catchments AT01, CZ01, CZ02 and NO01 exceeded this deposition threshold (10 kg ha−1 yr−1 = 71 meq m−2 yr−1) during 1990–2012. At these sites, the output fluxes of TIN were also elevated, compared to the other sites (Table 2). Likewise, Holmberg et al. (2013) found that the higher concentrations and fluxes in output of TIN were found at IM sites receiving the highest TIN deposition. Moreover, at IM sites where the critical loads of nutrient nitrogen were exceeded, they also showed higher TIN concentrations and fluxes in runoff. Ammonium concentrations in runoff in forested catchments are usually very low, due to effective microbial immobilization in the soil (e.g. Booth et al., 2005; Corre et al., 2007), and in many catchments (AT01, CZ01, CZ02, DE01, EE02, LT01, LT03 and SE14), NO3 clearly dominated the TIN flux (Table 2). Ammonium concentrations in runoff at the Norwegian sites NO01 and NO02 are also negligible, for which reason NH4 was not included in the chemical analysis in the runoff water chemistry monitoring program (de Wit, pers. comm.). At some sites, the flux of NH4 was larger than that of NO3 (FI01, LV02), albeit comparatively small, or the contribution of NH4 to the TIN fluxes was proportionally important (FI03, LV01, SE04, SE15, SE16, Table 2). This is likely due to catchment characteristics, such as hydrological flow paths, elevation gradients, and proportions of organic soils.

The present trend of TIN deposition at IM sites is decreasing, which should generally lead to decreased NO3 concentrations in
runoff (Forsius et al., 2005; Holmberg et al., 2013; Wright et al., 2001). TIN trends in runoff showed a mixed response with both positive and negative trend slopes, but at more than 50% of the sites, fluxes were decreasing rather than increasing. The previous trend assessment (1993–2006) for the 16 IM sites used in the present study (Vuorenmaa et al., 2009) showed significant decreases of NO₃ fluxes in runoff at four sites (C202, FI03, LT01 and LV02), while NO₂ flux increased significantly at five sites (DE01, FI01, LT03, NO02 and SE04). Thus, the trends for the output fluxes of TIN are still highly variable, indicating that surface water–watershed nitrogen dynamics are inherently complex, as nitrogen is strongly affected by biological processes, and nitrate concentrations in surface waters may highly fluctuate by season and spatially across ecosystems (e.g. Aber et al., 2003). Moreover, the short and long-term variations in the climate may mask long-term trends caused by N deposition (Wright et al., 2001). Nevertheless, the present trend in TIN output fluxes is decreasing at a majority of the sites, and significant increasing trends for NO₃ fluxes no longer occurred at the sites FI01, LT03 and NO02. Correspondingly, other surveys from Europe have not shown signs of a consistent and widespread increase in nitrate concentrations or exports in sensitive undisturbed freshwater (Garmo et al., 2014; Helliwell et al., 2014; Watmough et al., 2005; Wright et al., 2001). One might infer that the risk for nitrogen saturation is decreasing at these sites, because of the rather decreasing trend in NO₃ leaching. However, the leaching of inorganic N is only one signal of nitrogen saturation and may not be indicative in all sites (Lovett and Goodale, 2011). It should also be noted that studied IM catchments are hardly located in very high N deposition areas because inorganic N deposition in areas over the last decades rarely exceeded 100 meq m⁻² yr⁻¹ (ca 15 kg ha⁻¹ yr⁻¹), which can be considered as an intermediate N deposition level that is documented to increase the deposition-driven risk for elevated NO₃ leaching (e.g. Dise and Wright, 1995).

We detected a significant increase of TIN fluxes within the study period only at three sites (DE01, SE04 and SE14), but trends were likely not linked to the direct N deposition effects. At site DE01, a widespread and substantial forest dieback of Norway spruce (70% of the catchment area) due to bark beetle infestation (1997–2007) caused a high TIN output due to excess mineralization (Beudert et al., 2014). In January 2005, the site SE14 was hit by a severe storm, causing substantial damage to the forest by windthrow followed by a bark beetle infestation (~50% of trees killed/seriously affected in 2009), which substantially increased the variability and mean of the annual TIN output from 0.5–3.5 meq m⁻² yr⁻¹ (mean 1.3 meq m⁻² yr⁻¹) to 1.8–7.9 meq m⁻² yr⁻¹ (mean 4.5 meq m⁻² yr⁻¹) between the periods 1997–2006 and 2007–2012, respectively (data not shown). The disturbance regime caused increased inorganic N concentrations and NO₃ leaching at site SE14 from 2007 on (Löfgren et al., 2011), while at site DE01 – along with the recovery of forests – leaching of TIN started to decrease after 2007 (Beudert et al., 2014), which has consequently reduced the net loss of TIN in the catchment during the recent years (Fig. 3d). Löfgren et al. (2011) did not find any significant increases in inorganic N concentrations for the site SE04 in 1996–2009, and therefore the increase in NO₃ flux may be partly related to an increased runoff (7.8 mm yr⁻¹, p = 0.081) (Fig. 3h). The storm in 2005 also hit this site, but caused much less direct damage and bark beetle infestation than at site SE14 (Löfgren et al., 2011).

There may be several factors causing variation in TIN trends in IM catchments. While elevated TIN losses can be linked to high N deposition, trends and leaching losses of NO₃ may be highly variable between sites exposed to fairly similar levels of N deposition (Bringmark and Kvarnäs, 1995; Rothwell et al., 2008). The controls on nitrogen leaching are complex, as a result of the biogeochemical cycling of nitrogen in soils and N uptake by plants, and, therefore, also other factors than inorganic N deposition may largely modify TIN loss from forested catchments (Lovett and Goodale, 2011). These factors would include site characteristics (Brumme et al., 2008; Gundersen et al., 1998), climatic variables (Brookshire et al., 2011; Monteith et al., 2000; de Wit et al., 2008), acid deposition (Kopáček et al., 2013; Oulehle et al., 2011), denitrification (Wexler et al., 2014), soil organic N mineralization and nitrification (Kreutzer et al., 2009), immobilization (Booth et al., 2005: Corre et al., 2007) and disturbance legacies (Bernal et al., 2012; Dale et al., 2001). As an example, the Austrian site AT01 is a leaky karst catchment, where high inorganic N deposition causes a high nitrate loss, even if the forests are not N-saturated. The catchment has a fast runoff dynamic, and snowmelt periods and heavy rain events cause a strong throughflow, dictating not only annual, but also the long-term N budgets (lost et al., 2011). de Wit et al. (2008) reported increasing trends in NO₃ fluxes in runoff during the period 1973/1978–2005 at sites NO01 and NO02, which are located in high and low N deposition areas, respectively. These trends were unlikely dominated by soil N status and inorganic N deposition, but were more related to climatic variables, such as changes in snow depth, winter discharge and temperature. While continued decrease in N deposition is anticipated at the ICP IM sites in the future (Forsius et al., 2005; Holmberg et al., 2013), nitrogen continues to accumulate in catchment soils and vegetation, and concern remains that chronic N deposition may ultimately lead to biodiversity losses, decreased soil capacity to retain N and to an increased leaching of inorganic N. Our knowledge on the combined effects with changing climate and atmospheric CO₂ rise is also still limited.

In the present study, long-term annual variation in TIN concentrations in runoff was mostly associated with a variation in the TIN retention rate in the catchment, indicating the importance of various complex processes controlling inorganic N concentrations in drainage waters. Not all potential drivers (see e.g. Rothwell et al., 2008) were included in the empirical model in this study, and further analysis with specific landscape and soil data are needed to elucidate the variation in TIN concentrations and retention rates at IM sites. Moreover, considerable uncertainty remains with regard to the absolute size of the retention, as we did not account for gaseous losses out of the systems, a direct uptake of TIN or immobilization in the forest canopy, horizontal deposition or dry deposition in open field. Nevertheless, similar high levels of N retention (median > 90%) have been reported for forested catchments throughout Europe and North America (Kane et al., 2008; Watmough et al., 2005). An inorganic nitrogen retention rate was generally associated with the amount of TIN deposition, which corroborates results from ¹⁵N isotope studies showing that high N retention predominates in many different ecosystems, where the TIN supply is low (Templer et al., 2012).

Although the effects of anthropogenic nitrogen inputs on the dynamics of inorganic N in watersheds have been studied extensively, the influence of N enrichment on organic N loss is not as well understood (Pellerin et al., 2008). In pristine ecosystems with a low TIN deposition, total organic nitrogen (TON) dominates the terrestrial N export (e.g. Hedin et al., 1995). Studies comparing dissolved organic nitrogen (DON) losses from old-growth forests have reported that DON may account for 60–95% of the total dissolved nitrogen (TDN) losses from minimally disturbed watersheds (Perakis and Hedin, 2002; van Breemen 2002). The proportion of organic N loss in the total nitrogen loss at studied IM sites is considerable, varying generally from 60% to 94% (Vuorenmaa et al., 2013). Part of DON may decompose in the downstream surface waters or sea areas (releasing inorganic N compounds) and may thus contribute to detrimental N effects. Unfortunately, there was no sufficient DON data available from the IM sites to make a comprehensive analysis of long-term DON changes. However, it is evident that DON leaching in IM catchments needs further detailed studies, because climate change impacts on production and mineralization
of organic nitrogen and leaching of organic matter, and the potential risk for an elevated N loss from watersheds to surface waters, may also be anticipated in the future.

5. Conclusions
The ICP IM sites cover important deposition gradients in Europe, and the results from the ICP IM network document the positive effects of the international emission abatement actions in Europe, showing that runoff fluxes of SO$_4$ in forested catchments are decreasing and they have increasingly responded to the decreases in S emissions and deposition of SO$_4$ during the last 20 years. While SO$_4$ output fluxes are decreasing, an increasing net release of SO$_4$ (output $>$ input) has taken place in most of the IM catchments, showing that legacy deposits of atmospheric SO$_4$ deposition are mobilized to drainage waters. This indicates a recovery of the terrestrial ecosystems from atmospheric SO$_4$ loading, but may delay the recovery of surface waters from acidification. European nitrogen emissions have also decreased, which have resulted in a decrease of TIN deposition, but to a lesser extent than that of SO$_4$. Despite a decreasing deposition, trends in inorganic nitrogen fluxes in runoff were highly variable, but trend slopes were decreasing, rather than increasing. In general, TIN is effectively retained in the unmanaged IM forested catchments located in low or intermediate N deposition areas. However, the results of some of the sites also showed that confounding factors (factors other than direct deposition effects), such as severe disturbances in forested ecosystems (extreme climatic conditions, disease or infestation) can effectively disrupt the nitrogen cycle and enhance NO$_3$ leaching into surface waters. The disturbances in forest ecosystems caused by climate change and aging of European forests are anticipated to increase in the future (e.g. Dale et al., 2001; Seidt et al., 2014).

The more efficient retention of TIN than SO$_4$ results in generally higher leaching fluxes of SO$_4$ than those of TIN in European forested ecosystems. Proton budget calculations previously conducted at IM sites have indicated that SO$_4$ processes were generally the dominant source of actual soil acidification, despite the lower deposition inputs of SO$_4$, than inorganic N (Forsius et al., 2005). Besides changes in deposition, the variation in runoff contributed to the net release of mobilized SO$_4$ in IM catchments. The variation of TIN concentrations in runoff was mainly associated with a variation in the TIN retention rate in the catchment, and this, together with highly variable trends in TIN losses, indicate that a variation in inorganic nitrogen N leaching is controlled by complex processes that are not yet fully understood and needs further analysis. Deposited nitrogen continues to accumulate in catchment soils and vegetation, and may result in an enrichment of soil towards a state of N saturation in the long run. Because many of the S and N retention and release processes are also sensitive to changes in climatic variables, further analysis of processes regulating mobilization and the release of SO$_4$ and TIN in terrestrial ecosystems are needed to allow an evaluation of the effects, not only of emission reduction policies, but also of the changing climate. This study strongly emphasizes the importance of the integrated long-term monitoring of different ecosystem compartments for detecting the variety of impacts of changing environmental conditions on ecosystems.

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Appendix A. Supplementary data
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References

