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Nitrogen in surface waters: time trends and geographical patterns explained by deposition levels and catchment characteristics

Photo: Martin Pilote, Environment and Climate Change Canada

International Cooperative Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes

Convention on Long-Range Transboundary Air Pollution

LRTAP
Long-range Transboundary Air Pollution

Norwegian Institute for Water Research

REPORT

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Summary

The report presents a statistical analysis of controls (deposition, land cover, climate) on spatial variability and long-term trends (1992-2016) in surface water concentrations of nitrate (NO_3) and carbon to nitrogen (C/N) ratios of dissolved organic matter (DOM) at the ICP Water sites in Europe and North America. Nitrogen (N) deposition has declined over large parts of Europe and North America. Surface water NO_3 has decreased significantly at 46% of sites, increased at a few sites (4%) and has had no significant trend at the remaining sites. The C/N ratio of DOM has increased at 52% of the sites, decreased at 5% and has no trend at 43% of the sites. The greatest decline in surface water NO_3 occurred at sites with high N deposition and high NO_3 concentrations. The increase in C/N ratios of DOM is mainly related to increasing trends in total organic carbon (TOC) and seems largely unaffected by N deposition levels or trends. Data from most of the ICP Waters sites do not suggest that N saturation is occurring presently, but there is still a risk that climate change and ecosystem disturbances might cause higher N leaching in the future.

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CONVENTION OF LONG-RANGE TRANSBOUNDARY AIR POLLUTION

INTERNATIONAL COOPERATIVE PROGRAMME ON ASSESSMENT AND MONITORING EFFECTS OF AIR POLLUTION ON RIVERS AND LAKES

Nitrogen in surface waters: time trends and geographical patterns explained by deposition levels and catchment characteristics

Prepared at the ICP Waters Programme Centre
Norwegian Institute for Water Research
Oslo, May 2022

Preface

The International Cooperative Programme on Assessment and Monitoring of the Effects of Air Pollution on Rivers and Lakes (ICP Waters) was established under the Executive Body of the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP) in July 1985. Since then, ICP Waters has been an important contributor to document the effects of implementing the Protocols under the Convention. ICP Waters has prepared numerous assessments, reports and publications that address the effects of long-range transported air pollution.

ICP Waters and its Programme Centre is chaired and hosted by the Norwegian Institute for Water Research (NIVA), respectively. A programme subcentre is established at NORCE in Bergen. ICP Waters is supported financially by the Norwegian Ministry of Climate and Environment and the Trust Fund of the UNECE LRTAP Convention.

The main aim of the ICP Waters programme is to assess, on a regional basis, the degree and geographical extent of the impact of atmospheric pollution, in particular acidification, on surface waters. More than 20 countries in Europe and North America participate on a regular basis.

An important basis of the work of the ICP Waters programme is the data from existing surface water monitoring programmes in the participating countries, collected through voluntary contributions. The ICP Waters site network is geographically extensive and includes long-term data series (more than 25 years) for many sites. The programme conducts annual chemical intercomparison and biological intercalibration exercises.

This report presents a statistical analysis of controls (deposition, land cover, climate) of spatial variability and long-term trends (1992-2016) in surface water concentrations of nitrate (NO_3) and carbon to nitrogen (C/N) ratios of dissolved organic matter (DOM) at the ICP Water sites in Europe and North America. James Sample has been responsible for data compilation and trend analyses, Dag Hjermann has carried out the random forest statistical analysis, whereas Kari Austnes, Dick Wright and Øyvind Kaste have written the report.

We wish to thank the NFCs for their efforts on completing the records on catchment characteristics, N deposition and climate parameters from the various ICP Waters sites, and thereby making the present statistical analysis possible. We would also like to thank Michela Rogora (CNR IRSA) and Jakub Hruška (Czech Geological Survey) for valuable inputs to the draft version of this report, and Daniel Houle (Environment and Climate Change Canada) for providing the front-page photo.

Oslo, April 2022

Kari Austnes
Head of ICP Waters Programme Centre

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Summary

Surface waters in Europe and North America have been exposed to several decades of elevated nitrogen (N) deposition. Since the 1990s, N deposition has declined in many regions, but not to the same extent as sulphur deposition. Ecosystem N saturation has been a concern, but so far, no sign of region-wide increase in nitrate (NO_3) leaching has been observed. Results from the most recent ICP Waters trend report (Garmo et al. 2020) show that NO_3 has declined in all 12 ICP Waters regions, although many of the individual sites show no trend. The greatest declines were observed in the regions with the highest NO_3 levels. A few sites show increasing NO_3 concentrations, and this is probably due to site-specific factors or disturbances and not caused by the ambient N deposition levels as such.

The present report builds on the trend report by Garmo et al. (2020) and aims to explore possible explanatory factors for observed trends in NO_3, total organic N (TON) and the carbon/nitrogen (C/N) ratio of dissolved organic matter (DOM) at ICP Waters sites in Europe and North America over the past 25 years. With the latest efforts on completing the records on catchment characteristics, N deposition and climate parameters, it has been possible to perform a statistical analysis (random forest) of possible controls (deposition, land cover, climate) of spatial variability and long-term trends in concentrations of surface water NO_3 and C/N ratio of DOM. Based on the selection criteria there were 453 sites from 15 countries with valid NO_3 time series from 1992 to 2016, and 214 sites from six countries with NO_3, total nitrogen (Tot-N) and total organic carbon (TOC) concentration time series, needed to estimate TON and the C/N ratio of DOM, during the same period.

The random forest statistical analysis provides several measures of the relative importance of the different explanatory variables in splitting the sites based on the response variables, rather than providing a single test statistic or a p-value. Various combinations of explanatory variables were tested for the different random forest analyses. One challenge was that some of the catchment/land cover and climate variables were intercorrelated or varied systematically between continents/regions, in such a way that they were less suitable as explanatory variables in the statistical analysis.

The analysis of spatial variability of median 2012-2016 NO_3 concentrations in surface waters showed a strong positive relationship with N deposition level. Contrary to expectation, none of the land cover variables (forest, peatland, or sparsely vegetated land) emerged as important explanatory variables for the NO_3 concentration level at the regional scale. Possibly, the lack of explanatory power of land cover in the ICP Waters dataset is related to a predominance of forested sites in the dataset (about 50% of the sites have forest cover >75%) and differences in forest characteristics and N deposition history between regions represented in the ICP Waters network.

Over the period 1992-2016, surface water NO_3 concentrations decreased significantly at 46% of the ICP Waters sites, while they increased at 4% of the sites and had no significant trend at the remaining 50% of the sites. The statistical analysis showed that median NO_3 concentrations, median N deposition, and to a lesser degree percentage of coniferous forest and median TOC concentration, were important factors in explaining observed time trends in NO_3 concentrations. Hence, the greatest decline in surface water NO_3 concentrations occurred at sites with high N deposition and high NO_3 concentrations in surface waters. The high NO_3 concentrations in these lakes are probably related to a combination of atmospheric loading of N and relatively low catchment retention capacity, which makes them sensitive to changes in N deposition.

The analysis of spatial variability of median 2012-2016 TOC/TON ratios at the ICP Waters sites indicated that the median TOC concentration was the dominant explanatory factor. Median TON concentration, lake to catchment percentage and coniferous forest also appeared as explanatory variables, but much less important than TOC.

As N from long-term atmospheric deposition to varying degrees accumulates in catchments, one could expect a gradual enrichment of soil N stores, reflected in a decrease in the soil C/N ratio. This accumulation of N in the soil organic matter could in theory also affect the C/N ratio of DOM leached to surface waters. Decreasing trends in TOC/TON concentration ratios, however, occurred only at a few of ICP Waters sites. The TOC/TON mainly increased, or there was no significant trend. The trends in surface water TOC/TON ratios showed no significant relationship with current levels or trends in N deposition, and nor did the trend in surface water TON.

Not surprisingly, the random forest analysis indicated that the probability of increasing TOC/TON trends is highest at sites with high and increasing TOC concentrations, whereas increasing TON trends point in the opposite direction. Sites with a high percentage of coniferous forest show a higher probability of increasing TOC/TON trends, which could also be expected, as coniferous forest is positively correlated with both median TOC and TON. We speculate that the observed increase in TOC is associated with a change in organic matter quality, which impacts the C/N ratio of DOM.

It is difficult to document a lowering of the soil C/N ratio as a result of chronic exposure to elevated N deposition. Although some evidence exists for a relationship between N deposition levels and soil C/N ratios on large spatial scales, there are few studies that have documented changes in soil C/N ratios and/or TON leaching on a long-term temporal scale. There are also several other factors that can affect C/N ratios in soil and TOC/TON ratios in runoff water and thereby mask possible effects of accumulated N from atmospheric deposition; e.g., recently documented denitrification losses from forest soils, upward TOC trends due to reduction in sulphate deposition, re-allocation of N within the soil profile, or altered processing of C and N related to changes in climate, land use or vegetation cover.

Results from the present analysis of ICP Waters data are consistent with previous studies that have pointed at a N deposition "threshold" of about 10 kg N ha^{-1} yr^{-1}, below which very little NO_3 is leached. N deposition has declined in large parts of Europe and North America. Consistent with the pattern in deposition, concentrations in NO_3 also show a significant regional decline, even though many individual sites show no trend.

Long-term deposition of N and associated soil enrichment of N, leading to reductions in the C/N ratio in soil organic matter, have been hypothesized to lead to ''N saturation'' in the long run, with elevated leaching of NO_3 to stream waters. As data from a large share of ICP Waters sites show decreasing NO_3 trends in surface waters and an increase in the C/N ratio of DOM, there are few indications that N saturation is occurring here and now. However, there are sites with old-growth or disturbed forests in high-deposition areas that can be at risk. Also, climate change can pull in both directions; increased primary productivity due to increased temperature and longer growing season will imply a higher demand for N from plants and lower likelihood for N saturation, whereas more intensive rainfall, severe droughts and higher risk for insect attacks can promote higher N leaching from terrestrial ecosystems. Although the N deposition has been reduced in recent years, ambient loads might still exceed long-term sustainable levels and perhaps cause N saturation further into the future.

1 Introduction

Surface waters in Europe and North America have been exposed to several decades of elevated nitrogen (N) deposition. Since the 1990s, N deposition has declined in many regions, but not to the same extent as sulphur deposition (Tørseth et al. 2012; Du 2016). Ecosystem N saturation has been a concern, but so far, no sign of region-wide increase in nitrate (NO_3) leaching has been observed. On the contrary, recent regional studies indicate downward trends in surface water NO_3 concentrations (Eshleman et al. 2013; Garmo et al. 2014; Vuorenmaa et al. 2018; Garmo et al. 2020). However, the risk for high NO_3 leaching has been linked to soil N enrichment from N deposition, as indicated by the soil carbon/nitrogen (C/N) ratio (Anderson et al. 2002). In natural systems, a large fraction of N is usually transported from soils to streams in organic forms (Lepistö et al. 2021). Concentrations of dissolved organic matter (DOM) in surface waters have increased (Monteith et al. 2007; De Wit et al. 2021), and it is possible that this is associated with similar increases in organic N. A better understanding of controls of inorganic and organic N species is important for prediction of future leaching of N from catchment to surface waters.

In the most recent ICP Waters trend report, Garmo et al. (2020) presented trends in NO_3 concentrations at nearly 500 ICP Waters sites in Europe and North America for the period 1990-2016. The overall picture was that NO_3 has declined in all regions, although many of the individual sites show no trend. The greatest declines were observed in the regions with the highest NO_3 levels. An analysis of long-term data (1990-2015) from 25 forested catchments in the ICP Integrated Monitoring (IM) programme showed a similar pattern as the ICP Waters sites, with significantly decreasing concentrations of NO_3 in runoff at 50% of the sites (Vuorenmaa et al. 2018).

During the early 1990s there was a concern that the excess N from atmospheric sources would lead to "N saturation" of terrestrial ecosystems, resulting in increased leakage of NO_3 and acidifying components from soil to water (Aber et al. 1989; Stoddard 1994). Many natural or semi-natural terrestrial ecosystems, especially in central Europe and eastern North America, showed signs of N saturation during the 1990s with increased leaching of NO_3 (Wright et al. 2001; Kopáček et al. 2005). As demonstrated by recent analyses of long-term data from large, regional datasets as ICP Waters and ICP IM (Garmo et al. 2020; Vuorenmaa et al. 2018) many upland sites that received high N deposition loads during the 1970s and 1980s have experienced significantly reduced NO_3 concentrations in surface waters during the last 10-20 years (e.g. Oulehle et al. 2021a).

These observations are in line with results from large-scale roof experiments, where reduction or exclusion of N inputs at high-deposition sites resulted in rapid and large reduction in NO_3 concentrations in drainage water (Wright et al. 1993; Tietema et al. 1998). Taken together, these data do not indicate any immediate risk of N saturation, at least not in the short term. Future climate change might pull in different directions with respect to NO_3 losses from catchments: Deposition may increase/decrease (based on geographical position), due to increasing/decreasing rainfall and wash-out of pollutants from air (Hole and Enghardt 2008), whereas heavy rainfall after prolonged droughts may favor N flushing (Morecroft et al. 2000). Higher air temperatures might favor mineralisation and nitrification (van Breemen et al. 1998) but will also prolong the growing season and potentially result in greater plant uptake and less N leakage.

The present report builds on the findings in the trend report by Garmo et al. (2020) and aims to explore possible explaining factors for observed trends in NO_3 and the C/N ratio of DOM at ICP Waters sites in Europe and North America over the past 25 years. Data on N species concentrations

at the ICP Waters sites are analysed along with data on N deposition, climate and catchment properties to better understand what controls the variability in N trends and levels. More specifically, we quantify trends and geographical patterns in NO_3 concentration in surface waters. Additionally, we analyse temporal trends and spatial variability in C/N ratios of DOM in surface waters, as a proxy for N enrichment of catchment soils and elevated risk for N leaching losses to surface waters (cf. the N saturation hypothesis). We test if patterns in temporal trends and spatial variability can be explained by a combination of catchment properties, climate and N deposition trends. Moreover, we investigate how surface water chemistry can indicate possible N enrichment of catchment soils and risk of future N losses to surface waters.

2 Methods

2.1 Water chemistry data and sites selection

The ICP Waters database contains surface water data from around 20 countries across Europe and North America. The dataset now comprises 556 sites with long-term monitoring, predominantly located in "acid-sensitive" regions with low acid neutralising capacity and a history of acid deposition (Skjelkvåle et al. 2000). In 2019, much effort was put into completing records available for all sites, with particular emphasis on the period from 1990 to 2016 (Garmo et al. 2020). In 2020 the supporting catchment information was updated, quality checked and complemented, so that most sites now have information on catchment area, altitude and land cover.

The data were analysed with two different perspectives: Changes over time and geographical variability. The trend analyses were based on annual water chemistry (annual medians), while the spatial analysis was based on medians for 2012-2016 (median of annual medians), i.e. the most recent data included in this dataset.

When selecting sites for a particular analysis, there is always a trade-off between completeness of the data from the individual sites and geographical representativity. As an initial step, sites were selected based on the availability of water chemistry data, either for trend analyses or spatial analyses. The focus on the analyses was on NO_3 concentration and the TOC/TON ratio. TON is normally calculated as: TON = Tot-N – (NO_3 + NH_4). However, many sites lack time series data for ammonium (NH_4), so the number of sites could be increased markedly if NH_4 was assumed to be negligible. This is usually the case. A comparison of including or excluding NH_4 for sites with NH_4 showed that this had little effect on the trends (for 2000-2016, too few sites to compare trends for longer time periods), and the difference was small for median TON concentrations. Hence, it was decided to assume that TON = Tot-N - NO_3 with unit µg N/l.

The sites were thus generally selected based on the availability of NO_3, TOC and Tot-N data. In addition, some sites were excluded from selected analyses due to quality issues in the water chemistry data. It was also decided to exclude sites with more than 5% cultivated or urban land (see Chapter 2.2.1) in the catchment, since these sites are potentially affected by local sources of N.

For the trend analyses, the sites included have at least one year with data within both the first and last five years and overall at least 50% of the years with data for the relevant variable(s). The number of sites could be increased by choosing 1992 as start year rather than 1990, in particular for TOC/TON. Hence, the following sets of sites were chosen for the trend analysis:

- NO_3: Sites with valid NO_3 time series 1992-2016 (453 sites from 15 countries).
- TOC/TON: Sites with valid NO_3, Tot-N and TOC time series 1992-2016 (214 sites from 6 countries).

For the spatial analysis only sites with data from at least three years within 2012-2016 for the relevant variable(s) were selected. This gave:

- NO3: Sites with valid medians for NO_3 2012-2016 (446 sites from 15 countries).
- TOC/TON: Sites with valid medians for NO_3, Tot-N and TOC 2012-2016 (288 sites from 9 countries)

Most sites are lakes, but streams are also included. The sampling frequency varies markedly between sites, from weekly to annual, but this has not been considered in the site selection. There is little

information on detection limits available, so data have been selected irrespective of this. For observations below the detection limit, the detection limit is used. The dataset is dominated by sites in Canada, the US, Norway and Sweden. There are also several sites from Finland and the United Kingdom, but fewer from the remaining countries. Tables with the number of sites per country included in the various statistical analyses are displayed in chapter 3.

2.2 Other input data

2.2.1 Land cover

Land cover is given as % cover of different land cover types. These were redefined in March 2020 and a call was sent out for the ICP Waters' National Focal Centres to check and, if needed, update the data. A description of the different land cover categories was provided, largely with reference to Corine land cover definitions[1].

The different land cover categories are given in **Table 1**. For two main categories (total forest, total shrub/herbaceous) the countries were encouraged to submit data for sub-categories. If doing so they should not provide the total area for these sub-categories, which was calculated jointly across sites. For the current analysis it was decided to merge some of the land cover categories, to reduce the number of explanatory variables. The overlapping categories Total forest and the two forest sub-categories were never used in the same analysis. The category Other was not used in the analyses, as the cover was usually very low and the land cover it represents is unknown and difficult to interpret.

Table 1. Land cover categories in the ICP Waters database and those used in the current analysis

Land cover category ICP Waters database	Optional sub-category	Categories used for analysis
Urban		Urban
Cultivated		Cultivated
Total forest		Total forest
	Coniferous forest	Coniferous
	Deciduous forest	Deciduous/mixed
	Mixed forest	
Total shrub/herbaceous vegetation		Total shrub/herbaceous
	Grasslands	
	Heathlands	
	Transitional woodland/shrub	
Bare rock		Bare/sparse
Sparsely vegetated		
Glacier		
Wetland		Wetland
Lake		Lake/water
Water excluding lake		
Other		

[1] https://land.copernicus.eu/user-corner/technical-library/corine-land-cover-nomenclature-guidelines/html

2.2.2 Deposition

As a measure of general deposition level during the time period studied, both the median and the accumulated annual deposition could be used. Since these were well correlated, it was decided to use the median deposition, as it is easier to relate to these values. Annual N deposition data were acquired in three different ways, for Europe, the United States and Canada, respectively.

Europe

For 2000-2016 annual deposition data as estimated by the EMEP[2] model was used. The model is a chemical transport model modelling deposition based on emissions data (Simpson et al. 2012; Tsyro et al. 2018). Data are available on a 0.1 x 0.1 long-lat grid[3] . The data for 1990-1999 are on a 0.50 x 0.25 long-lat grid and computed with source-receptor matrices provided by EMEP for CIAM[4], using country emission generated with the GAINS[5] model (see Schöpp et al. 2003). Data were assigned to each site by bi-linear interpolation between the four nearest grid values (the corners of the grid cells).

United States

For 2000-2016 the TDEP dataset was used (annual data). TDEP is based on of wet deposition measurements from the NADP National Trends Network (NTN) and estimates of dry deposition using a method that combines ambient air monitoring data with output from the Community Multiscale Air Quality (CMAQ) modelling system. The resolution is 4 km (4.134-km actual distance). For 1990-1999 total deposition was calculated from the annual NADP wet deposition (modelled, spatial interpolation (IDW) of quality-controlled point observation data from NTN sites, resolution 2 km (2.338-km actual distance)), and dry deposition based on the wet/dry deposition ratio calculated for each grid cell from the TDEP 2000-2004 mean wet and dry deposition. Data were downloaded from the US EPA[6] Critical Loads Mapper[7]. Each site was assigned the deposition of the grid cell in which it was located.

Canada

The total (wet + dry) N deposition was estimated using modelled total N deposition to all sites in 2010 (with the ADAGIO framework, which is a fusion of modelled and observed fields). The long-term trend was estimated from trends at several CAPMoN stations. Total deposition was available for each station on a 5-year average. The mid-point of each period and linear interpretation was used to estimate annual deposition from 1989 to 2016. These long-term trends were normalised to 2010, and then each site was allocated to one or more of these trend patterns. In some instances, sites were located between two stations, so the distance was used to produce a weighted average trend.

2.2.3 Climate

Temperature and precipitation data from the CRU dataset (University of East Anglia Climatic Research Unit; Jones and Harris 2008) were downloaded from the British Atmospheric Data Centre[8].

[2] Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe
[3] https://emep.int/mscw/mscw_moddata.html
[4] Centre for Integrated Assessment Modelling
[5] https://iiasa.ac.at/web/home/research/researchPrograms/air/GAINS.html
[6] United States Environmental Protection Agency
[7] https://clmapper.epa.gov/
[8] http://badc.nerc.ac.uk/data/cru/

These are monthly values, available on a 0.5 x 0.5 degree grid. The data were aggregated to annual data by averaging (temperature) or summing (precipitation) and each site was assigned the data for the grid cell in which it was located.

2.3 Statistical analysis

2.3.1 Trend analysis

Trends for the time period 1992-2016 were analysed for each individual time series of annual data. For the trend analysis, the Mann-Kendall test was applied (Hirsch and Slack 1984). The test identifies monotonic trends and is robust against outliers and missing data and does not require normal distribution of data. Slopes were calculated using the Sen estimator (Sen 1968). Trends were analysed for the main chemical variables (NO_3, TOT-N, TOC, TON, TOC/TON), as well as temperature, precipitation and N deposition.

2.3.2 Random forest analysis

Background

Random forest analysis was aimed at explaining differences in trends or 2012-2016 median levels between sites. The random forest algorithm (Breiman 2001) is an extension of the decision-tree method. Decision trees is a classification method which seeks to explain the response variable using a set of predictor variables (which can be both categorical and continuous; Breiman et al. 1984). In the simplest form of decision-tree analysis, the first step is to search for the variable x which best explains the response variable by splitting the data by a value a (data with $x < a$ and data with $x > a$). This first split of the data is called the root node. After the data have been split in two, the procedure may be repeated for each branch, until some specified criterion has been met. This results in a "tree" of decisions (**Figure 1**). Decision-tree methods are good at handling interaction effects among variables; however, they tend to overfit to the data, i.e., they are overly affected by the particular data set to which they are fit.

Figure 1 gives an example of a decision tree. Here the response variable is a numeric variable (median NO_3 concentrations), and the analysis aims to find the explanatory variable and the value of this variable that gives the best split of the data with respect to the response variable, i.e., the value which results in as little variance in each subset as possible. In this case, the first split is to separate sites with temperature ("tmp" in the figure) above 9°C from sites with temperature below 9°C. The high-temperature subset results in a fairly homogenous group with regard to NO_3 concentrations (mostly low concentrations, 100-300 µg N l^{-1}), while the low-temperature subset is split several times using other variables. The same explanatory variable may be used in several splits, as is the case for "median_toc".

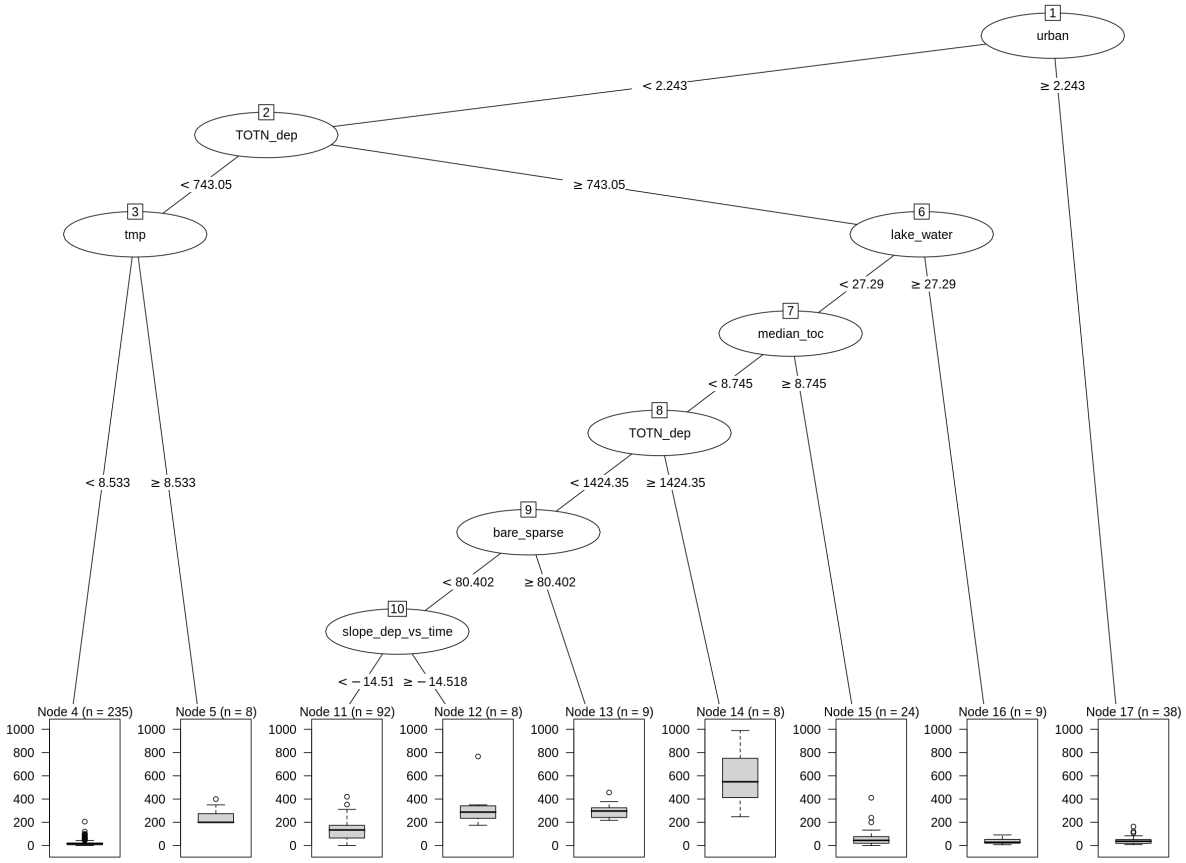

Figure 1. Example of a classification tree from a random forest analysis. Here the response variable is the median NO_3 concentration 2012-2016, i.e. the same analysis as performed using random forest in chapter 3.1.2. The bars at the bottom show the terminal nodes, i.e. the final subdivision of the data, and the small boxplots show the variation of median NO_3 within each part of the subdivided data. For instance, the sites with lowest median NO_3 values are the ones with TOTN_dep<712.67. The decision tree analysis used in this case was created by an evolutionary algorithm (the R package evtree, Grubinger et al. 2014). A random forest analysis is an ensemble of a large number of such trees.

Single decision trees incorporate interactions between variables, and they are easy to interpret. However, they give no information about the uncertainty of the model and whether small changes in the data could have given a very different tree. The random forest algorithm addresses this by producing a large number of trees (e.g. 500 trees), where the data used to make each tree differ slightly in two ways, by permutation of variables and permutation of samples. 1) Permutation of variables: At each split, the algorithm randomly selects a subset of explanatory variables which can be used as candidates for splitting the data. This prevents the multitude of decision trees from relying on the same set of features and the individual trees are decorrelated. 2) Permutation of samples: Each tree draws a random sample of data from the training dataset when generating its splits. This introduces a further element of randomness, which prevents the individual trees from overfitting the data. The response variable can be categorical or continuous; in our case, we have only used continuous response variables, where the goal of the analysis is to explain as much of the variance in the response variable as possible (as in, e.g., multiple regression).

The random forest analysis does not provide a single test statistic or a p-value. Rather, it provides different measures of how important the different explanatory variables are in splitting the sites

based on the response variables. These are visualised in so-called multi-way importance plots. For a given explanatory variable *x*, the following measures of importance can be calculated:

1. *times_a_root*: How often variable *x* is the selected for the first split (the 'root' of the tree).
2. *mean_min_depth*: The 'minimum depth' of a variable in one tree is the level where it first was used (e.g. 'median-toc' has level 3 in **Figure 1**). Then the mean of 'minimum depth' across trees is calculated. Thus, this measure is related to 'times_a_root': If 'times_a_root' is low and 'mean_min_depth' is high, it means that this variable is important for only a subset of the data (after the dataset first has been split using other variables).
3. *no_of_nodes*: Total number of splits based on variable *x*
4. *node_purity_increase*: The average decrease in sum of squares in the splits based on variable *x*
5. *mse_increase*: The average *increase* in mean sum of squares when variable *x* is *not* used in the analysis (see "permutation of variables" above)
6. *p_value*: P-value for a one-sided binomial test to test whether the number of successes (i.e. nodes where variable *x* is used for splitting) is higher than the theoretical number of successes if they were random.

In the results, we plot all these six measures of importance using two plots, one plot showing 1-3 and another showing 4-6. The plot shows one point for each explanatory variable, but only the six best variables (according to all measures plotted) are labelled ("top"; in some cases, seven variables are labelled because the variables six and seven were equally important).

Another way to visualise the results is by plotting the prediction using two selected variables *X* and *Y*. We use the random forest to predict the outcome for a certain combination of *X* and *Y* values, letting all remaining predictors be sampled from their empirical distributions. This is repeated for a range of values for *X* and *Y*, and the predicted values are shown using colours. As the effect of other variables is "removed" by drawing random values, this is called the *partial effect of X and Y*. In the figures shown in the results, we have made predictions for two predictor variables at a time, making a 'map' where the colours of each cell indicate the effect on the response variable for the given combination of values. The sites are added in the same plots, using the actual values of the explanatory variables, showing how the sites are distributed within this variable space. White areas in these plots represent non-existent combinations of the two variables.

Analyses

Random forest analysis was run for median NO_3 and TOC/TON (2012-2016), and for time trends in NO_3 (1992-2016) and TOC/TON (1992-2016). In all analyses, the response variable was continuous (in the case of trends, we used the Sen slope as the response variable). We used R version 4.1.2 and the packages randomForest 4.6-14 (Liaw and Wiener 2002) and randomForestExplainer_0.10.1 (Paluszynska et al. 2020) for fitting models and making the figures for variable importance and partial effects. 500 trees were fitted in each analysis, and the number of variables randomly sampled as candidates at each split was p/3 where p is the number of explanatory variables). The minimum size of the terminal nodes (see **Figure 1**) was 5 and trees were grown until maximum size.

The full set of explanatory variables used is given in **Table 2**. Some variables were always included, while some were only included for certain analyses: Land cover was considered relevant in all analyses, reflecting both N retention capacity, soil depth and soil organic matter quality. Median precipitation and temperature for the time period 1992-2016 were included as measures of general climate conditions, while the slopes were considered relevant only when looking at trends in the

response variable. Median N deposition 1992-2016 reflected the overall deposition level, while the slope was considered to be able to affect both trends and current (2012-2016) conditions. Relevant median water chemistry was included for the same time period as the response variable.

Table 2. Explanatory variables used in the random forest analyses. (X) indicates that the variable was considered and tested for the analysis, X that it was selected

Explanatory variable	**Variable code**	**Unit**	Median NO_3 2012-16	Trend NO_3 1992-16	Median TOC/TON 2012-16	Trend TOC/TON 1992-16
Urban	urban	%	X	X	X	X
Cultivated	cultivated	%	X	X	X	X
Total forest	total_forest	%	(X)	(X)	(X)	(X)
Coniferous	coniferous	%	X	X	X	X
Deciduous/mixed	decid_mixed	%	X	X	X	X
Total shrub/herbaceous	total_shrub_herbaceous	%	X	X	X	X
Bare/sparse	bare_sparse	%	X	X	X	X
Wetland	wetland	%	X	X	X	X
Lake/water	lake_water	%	X	X	X	X
Catchment area	catchment_area	km^2	(X)	(X)	X	X
Altitude	altitude	m	(X)	(X)	(X)	(X)
Annual precipitation, median 1992-2016	pre	$mm\ yr^{-1}$	X	X	X	X
Sen slope precipitation, 1992-2016	slope_pre	$mm\ yr^{-1}$		X		X
Annual average temperature, median 1992-2016	tmp	^oC	X	X	X	X
Sen slope temperature, 1992-2016	slope_tmp	$^oC\ yr^{-1}$		X		X
Annual N deposition, median 1992-2016	TOTN_dep	$mg\ N\ m^{-2}\ yr^{-1}$	X	X	X	X
Sen slope N deposition, 1992-2016	slope_dep_vs_time	$mg\ N\ m^{-2}\ yr^{-2}$	X	X	X	X
NO_3 concentration, median 1992-2016	NO_3	$\mu g\ N\ l^{-1}$		X		
TOC concentration, median 1992-2016	TOC	$mg\ C\ l^{-1}$		X		X
Sen slope TOC conc, 1992-2016	slope_toc_vs_time	$mg\ C\ l^{-1}\ yr^{-1}$	(X)	X	(X)	X
TOC concentration, median 2012-2016	median_toc	$mg\ C\ l^{-1}$	X		X	
TON concentration, median 1992-2016	TON	$\mu g\ N\ l^{-1}$				X
Sen slope TON conc, 1992-2016	slope_ton_vs_time	$\mu g\ N\ l^{-1}\ yr^{-1}$				X
TON concentration, median 1992-2016	median_ton	$\mu g\ N\ l^{-1}$			X	
TOC/TON, median 1992-2016	TOCTON	$g\ g^{-1}$				X

Apart from these fixed choices, various combinations of explanatory variables were tested for the different analyses. There was a trade-off between excluding variables to include more sites and not excluding variables that proved important. Also, in some cases including or excluding variables did

not affect the number of sites, but it highly affected the analysis results. Here the inclusion/exclusion was decided based on the effect on the interpretation.

For forest, parallel analyses were made using either total forest or the two sub-categories. Using total forest made it possible to include slightly more sites in the analysis. However, as it turned out that coniferous and deciduous/mixed forest had different explanatory powers, it was decided to use only the forest sub-categories in the analyses. Altitude proved to be important in some analyses, while less so in others. However, the interpretation of this variable is difficult, as it is a composite variable reflecting both land cover, temperature, precipitation, and in some cases N deposition. Since these other variables were already included, it was decided to exclude altitude.

3 Results

3.1 Nitrate

3.1.1 Data overview

Catchment characteristics

The ICP Waters sites cover a large gradient in climate, N deposition levels and NO_3 concentrations in water (**Table 3**). Annual mean temperatures vary between -3 and 11°C, and annual precipitation range from < 500 to nearly 3500 mm yr^{-1}. Median N deposition during 1992-2016 ranged from < 100 to 3500 mg N m^{-2} yr^{-1}, whereas NO_3 concentrations in water ranged from 0 to nearly 1000 µg N l^{-1}.

The sites represent a large diversity with regard to catchment size and land cover. Most catchments are small (median: 3 km^2), but the size distribution varies from < 1 to nearly 2000 km^2. The dominant land use is coniferous or deciduous forests (~50% of the sites have forest cover >75%) but some catchments also include more open areas with wetlands, shrubs or sparsely vegetated areas with scattered elements of bare rock. A majority of the catchments contain lakes. Among the 434 sites with land cover data, the median lake or open water percentage is 12. Sites with more than 5% cultivated land or urban areas in their catchments were excluded from the dataset.

Median N deposition

The regional variation in N deposition (median 1992-2016) is shown on maps in **Figure 2**. In North America, the highest levels (>750 mg N m^{-2} yr^{-1}) are found in the central and eastern parts. All sites in the northern regions (Quebec, Nova Scotia, Maine) had median N deposition below 750 mg N m^{-2} yr^{-1}. In Europe, the highest levels (>750 mg N m^{-2} yr^{-1}) are found in central/eastern Europe, large parts of the UK and in the southern parts of Scandinavia. The lowest N deposition levels are found in the middle and northern parts of Scandinavia, the western parts of Ireland and the northern parts of Scotland.

Median NO_3 concentrations

The spatial distribution of surface water NO_3 concentrations is relatively similar to the regional N deposition pattern (**Figure 3**). One exception was the Irish sites, which had relatively high NO_3 concentrations in surface water, despite relatively low N deposition levels.

The relationship between surface water NO_3 concentrations and N deposition levels is further illustrated in **Figure 4**. Apart from the Irish sites, NO_3 concentrations in water remain relatively low (< 125 µg N l^{-1}) until N deposition levels exceed 750 mg N m^{-2} yr^{-1}. This may seem like a threshold after which there is a steep increase in sites with higher NO_3 concentrations. Three Dutch sites deviate from this general pattern by having low surface water NO_3 concentrations despite N deposition levels in the range 2500-3500 mg m^{-2} yr^{-1}. These sites have more than 50 % lake/water in the catchment.

Table 3. Range in site characteristics, NO_3 concentration and N deposition. There are 446 sites with valid median NO_3 concentration 2012-2016. Some of the sites lack other types of information.

	Unit	N	Min	1st quartile	Median	3rd quartile	Max
NO_3 concentration, median 2012-2016	µg N l^{-1}	446	0*	14	28	94	988
Annual N deposition, median 1992-2016	mg N m^{-2} yr^{-1}	446	72	420	602	854	3503
Catchment area	km^2	373	0	1	3	10	1985
Altitude	m	446	2	128	278	553	2387
Annual precipitation, median 1992-2016	mm yr^{-1}	446	481	760	1107	1351	3473
Average annual temperature, median 1992-2016	°C	446	-3	4	5	7	11
Urban	%	434	0	0	0	1	5
Cultivated	%	434	0	0	0	0	5
Coniferous forest	%	434	0	2	18	65	100
Deciduous/mixed forest	%	434	0	1	14	54	96
Shrub/herbaceous vegetation	%	434	0	0	2	13	100
Wetland	%	434	0	0	2	6	87
Lake/water	%	434	0	6	12	20	95
Bare rock/sparsely vegetated	%	434	0	0	0	0	97

** For some US sites all 2012-2016 nitrate values were below the detection limit and set to zero by the country*

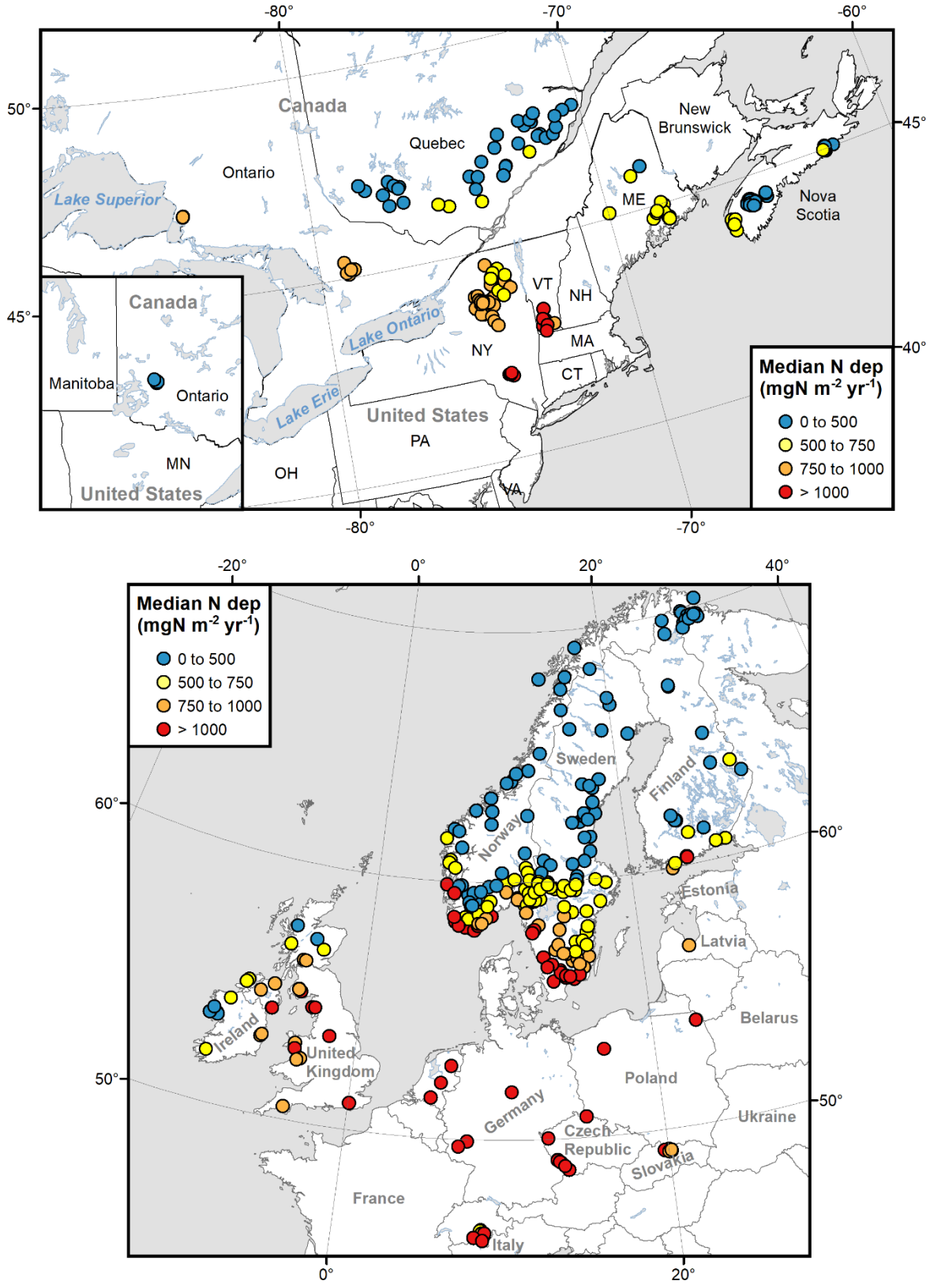

Figure 2. Map of median N deposition 1992-2016 at the 446 sites with valid median NO_3 concentration 2012-2016.

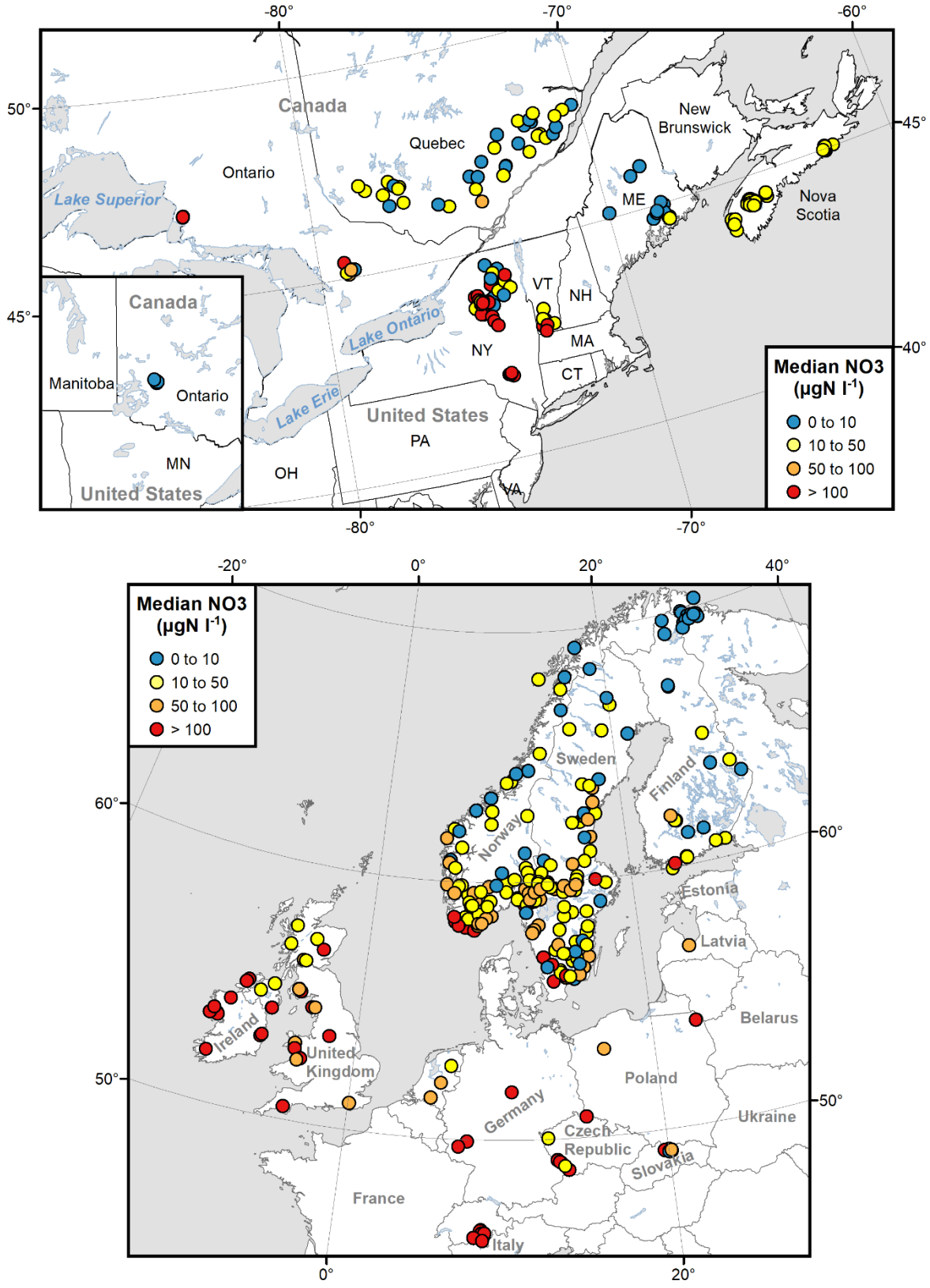

Figure 3. Map of median NO_3 concentration 2012-2016 at 446 sites with valid median.

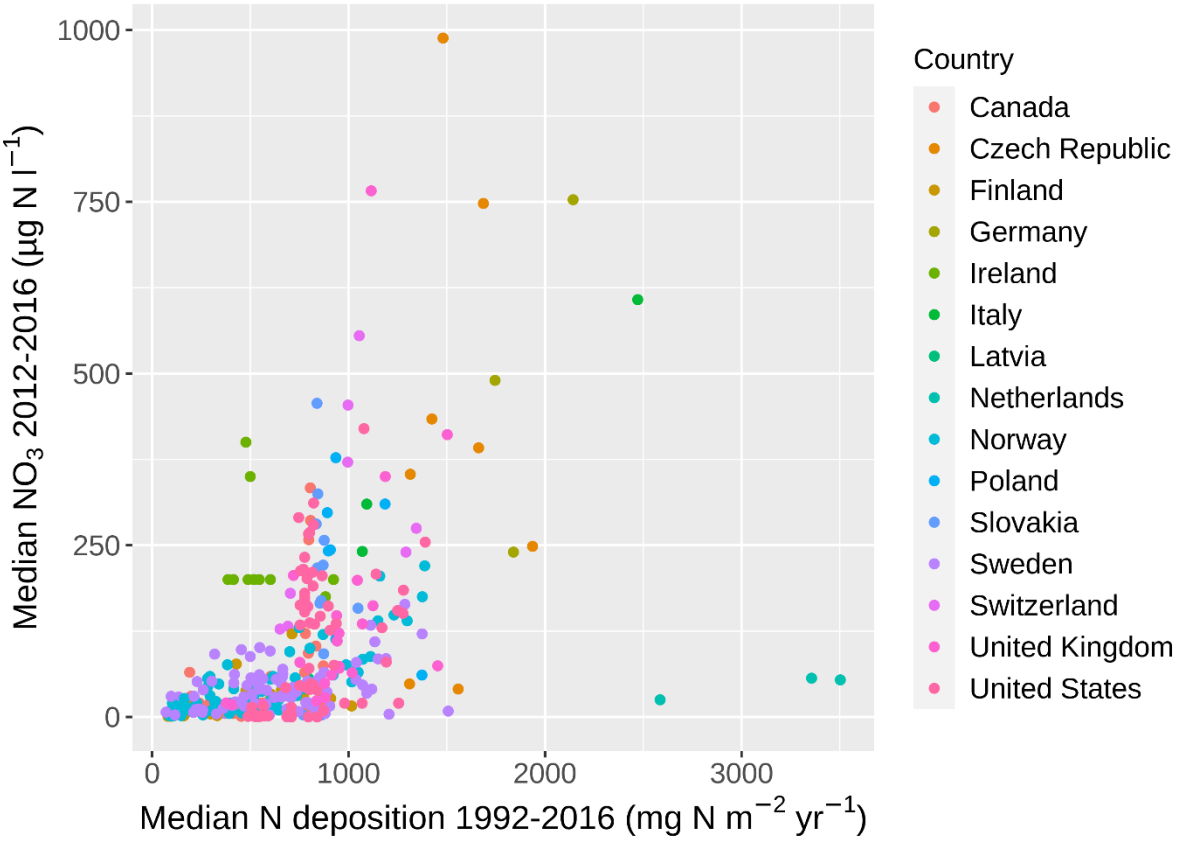

Figure 4. Median NO_3 concentration 2012-2016 vs median N deposition 1992-2016 at the 446 sites with valid median NO_3 concentration data 2012-2016.

N deposition trends

A vast majority of the ICP Waters sites show a significant decreasing N deposition trend during the 25 years from 1992 to 2016 (**Figure 5**). As could be expected, the largest change in absolute numbers (mg N m^{-2} yr^{-1}) was generally recorded at sites with the highest initial N deposition (cf. **Figure 2**). The largest absolute reductions (more than 50 mg N m^{-2} yr^{-1}), expressed by the Sen slope, were found in Central Europe and in the southernmost part of Norway.

NO_3 concentration trends

Although many sites show decreasing trends in surface water NO_3 concentrations (yellow and blue dots in **Figure 6**), there are also sites with increasing trends (orange and red dots). The largest decrease (in µg N l^{-1} yr^{-1}) is in south and eastern Germany and in parts of the Czech Republic. Sites with increasing concentrations are in the north-eastern USA, southwestern parts of the Czech Republic, in parts of Sweden, and at single sites in Finland, Latvia, UK and Ireland. Of the 453 sites in the dataset, NO_3 concentration decreased significantly at 210 sites, while it increased significantly at only 19 sites (**Figure 6**, **Figure 7**). At the remaining 224 sites there was no significant trend. The median Sen slope across all sites was -0.37 µg N l^{-1} yr^{-1}. At the ICP Waters sites with significantly decreasing concentrations, the change in surface water NO_3 concentrations (in µg N l^{-1} yr^{-1}) was positively related with the median NO_3 concentrations (**Figure 7**).

Of the 19 sites with statistically significant increases in NO_3 concentration, two sites (Bohemian Forest, Czech Republic and Bayerische Wald, Germany) have very high median NO_3 concentrations (>

600 µg N l^{-1}). All the other 17 sites had median NO_3 concentrations 1992-2016 < 100 µg N l^{-1}. Two of the sites (one in Ireland and one in Latvia) had > 50% wetlands. The Irish site also had a high proportion of bare/sparsely vegetated land. Thirteen of the sites are located in forests in southern Sweden (7 sites), southern Finland (2 sites) or Vermont in eastern US (4 sites). Six of the Swedish and one of the Finnish sites have more than 2% urban plus cultivated land in the catchment and are thus potentially influenced by direct human activities. Only one site (in the UK) is dominated by the land cover type shrub/herbaceous.

The largest decreases in surface water NO_3 concentrations appear at sites with median N deposition between 750 and 2000 mg N m^{-2} yr^{-1} (**Figure 8**). These were also the sites with the highest median NO_3 concentrations in water (cf. **Figure 4**). The German dataset shows a large variability in Sen slope estimates among sites, even though the N deposition level is relatively uniform. Three of the Italian sites have particularly high and strong decreasing N deposition, but no change in NO_3 concentration.

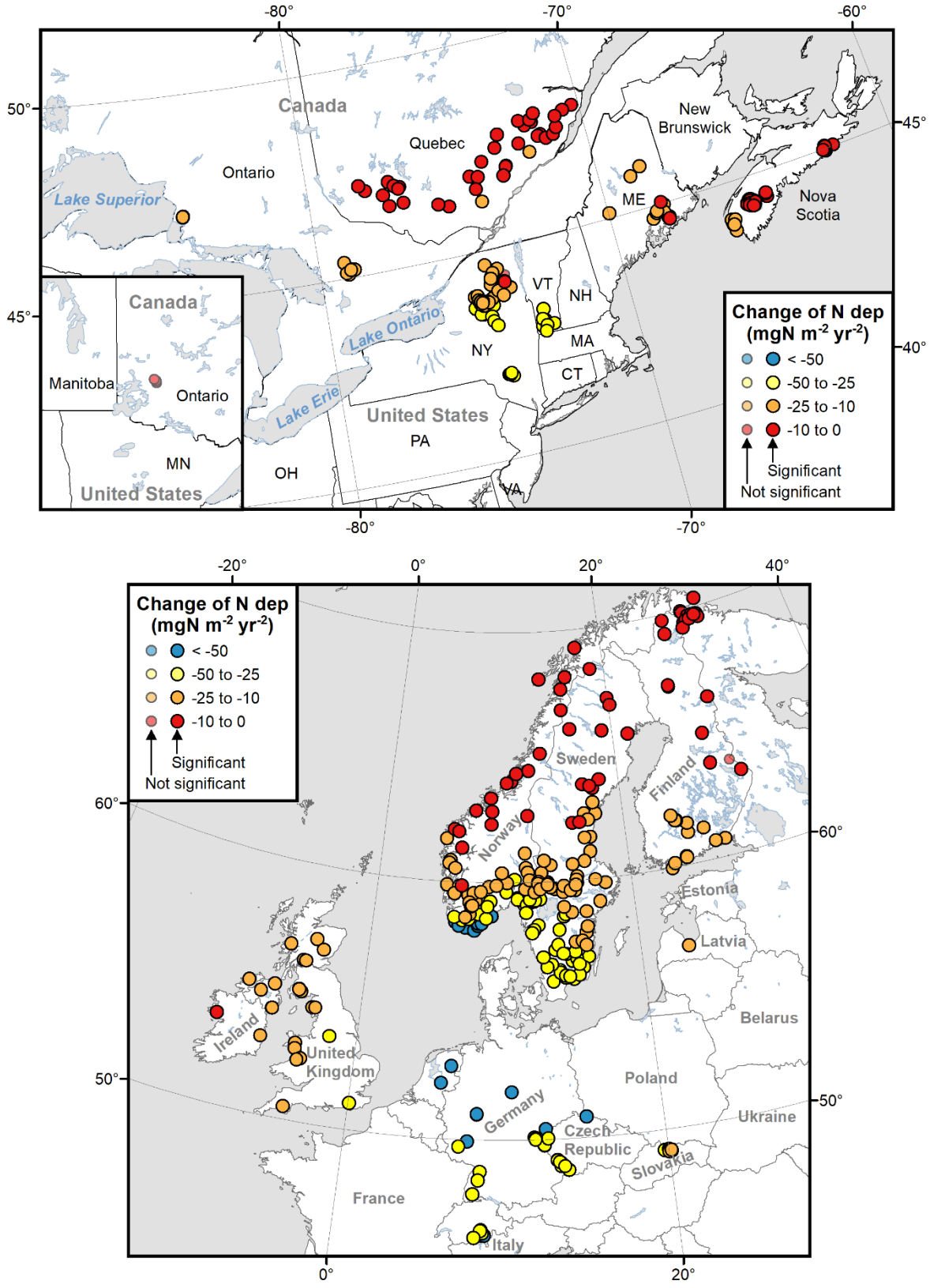

Figure 5. Map showing trends in N deposition 1992-2016 at the 453 sites included in the analysis of NO_3 concentration trends.

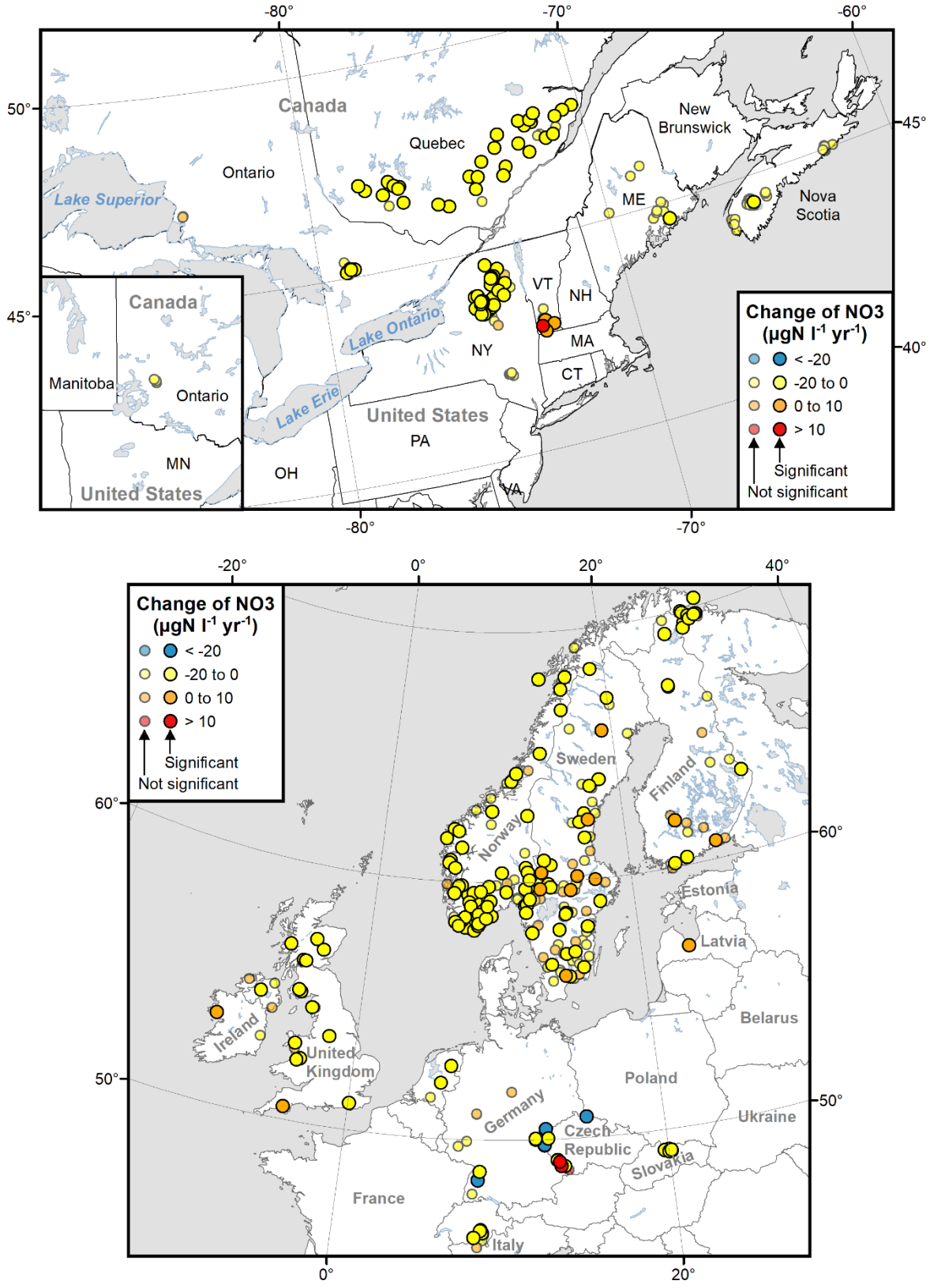

Figure 6. Map showing trends in surface water NO_3 concentration 1992-2016 at the 453 sites included in the analysis of NO_3 concentration trends.

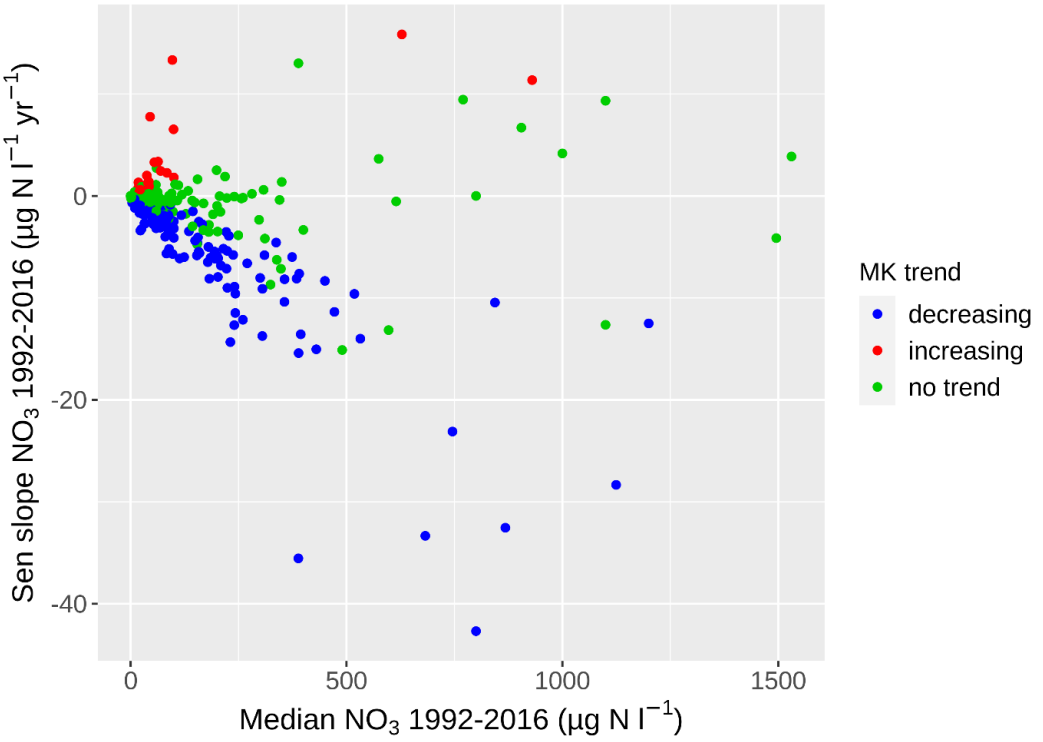

Figure 7. Trend vs median NO_3 concentration 1992-2016. The colour indicates the significance level of the Mann-Kendall trend test at the 453 sites.

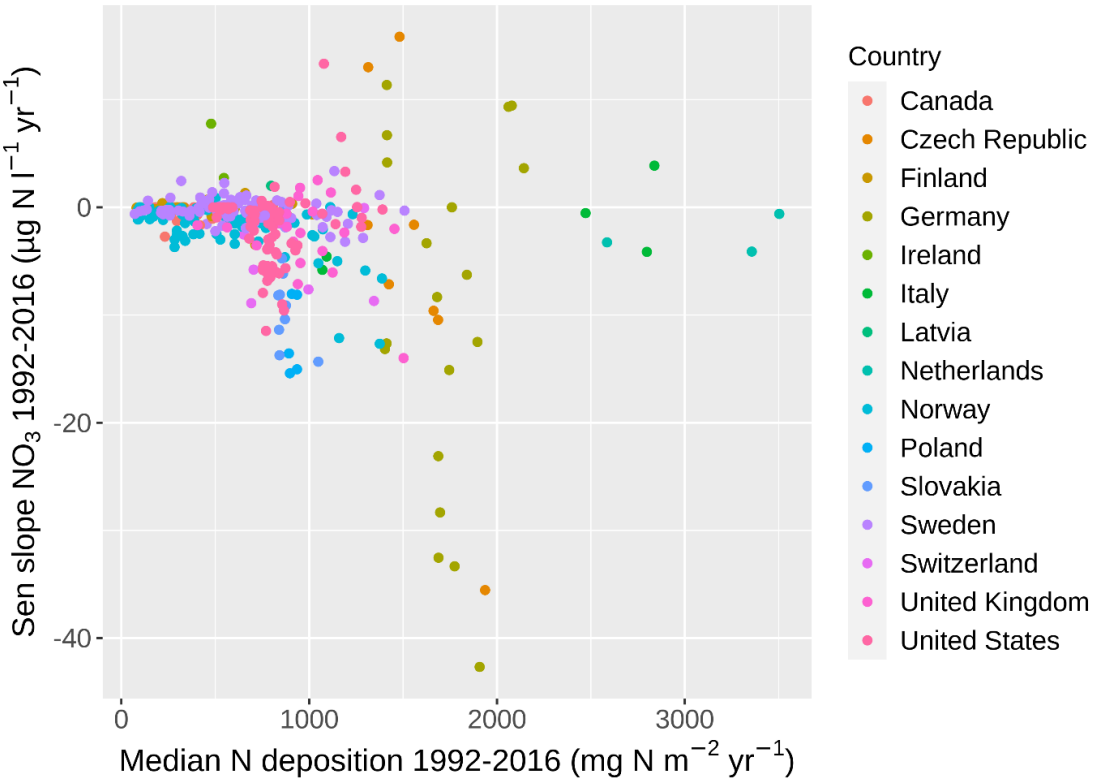

Figure 8. NO_3 concentration trend vs median N deposition 1992-2016 at the 453 sites.

3.1.2 Spatial variability of median NO_3 concentrations 2012-2016

The random forest analysis aims to explain the observed present-day geographic distribution of median NO_3 concentrations 2012-2016 at the ICP Waters sites. The explanatory variables included in the analysis are listed in **Table 2**.

Site selection

Catchment area was not included because this would decrease the number of sites available for the analysis substantially (to 350). For example, none of the US sites had data for catchment area. Besides, when included, catchment area did not prove to be an important variable. Of the 446 ICP Waters sites with median NO_3 data, 431 had data for all the explanatory variables used in the analysis. Three sites were excluded due to lacking median TOC concentrations and 12 sites were excluded as they did not have forest cover split into sub-categories. The sites included or excluded from the analysis are listed by country in **Table 4**.

Table 4. Sites included in or excluded from the analysis, by country

	Excluded	Included
Canada	4	103
Czech Republic	0	8
Finland	0	22
Germany	0	3
Ireland	0	10
Italy	0	3
Latvia	0	1
Netherlands	1	2
Norway	0	80
Poland	2	5
Slovakia	0	12
Sweden	0	87
Switzerland	8	0
United Kingdom	0	22
United States	0	73
Total	**15**	**431**

Results from random forest analysis

As shown in **Figure 4**, there is a positive relationship between NO_3 concentration and N deposition. The strong influence of N deposition on the spatial variation in NO_3 concentration is also shown by the random forest analysis, as depicted in the correlation matrix for the explanatory variables (**Figure 9**) and two multi-way importance plots (**Figure 10**).

None of the catchment characteristics used as explanatory variables are nearly as important as N deposition. The median N deposition is also strongly correlated with the time trend in N deposition (**Figure 11**). None of the land cover variables appear to systematically explain the NO_3 concentration level. Temperature shows some importance, but this seems to be related to the strong correlation with N deposition (**Figure 13**; **Figure 12**).

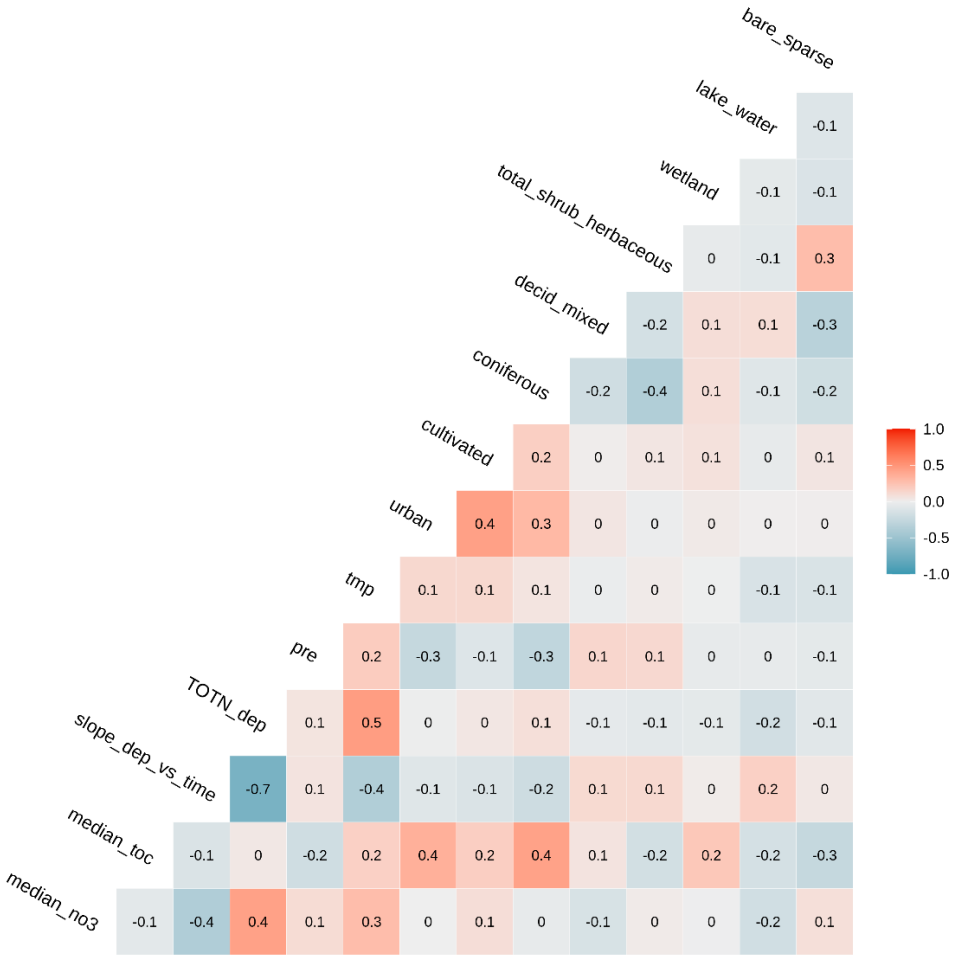

Figure 9. Correlation matrix for the explanatory variables and the response variable (median_no3) used in the analysis of median NO_3 concentrations 2012-2016 at 431 ICP Waters sites (cf. **Table 2** for explanatory variable names).

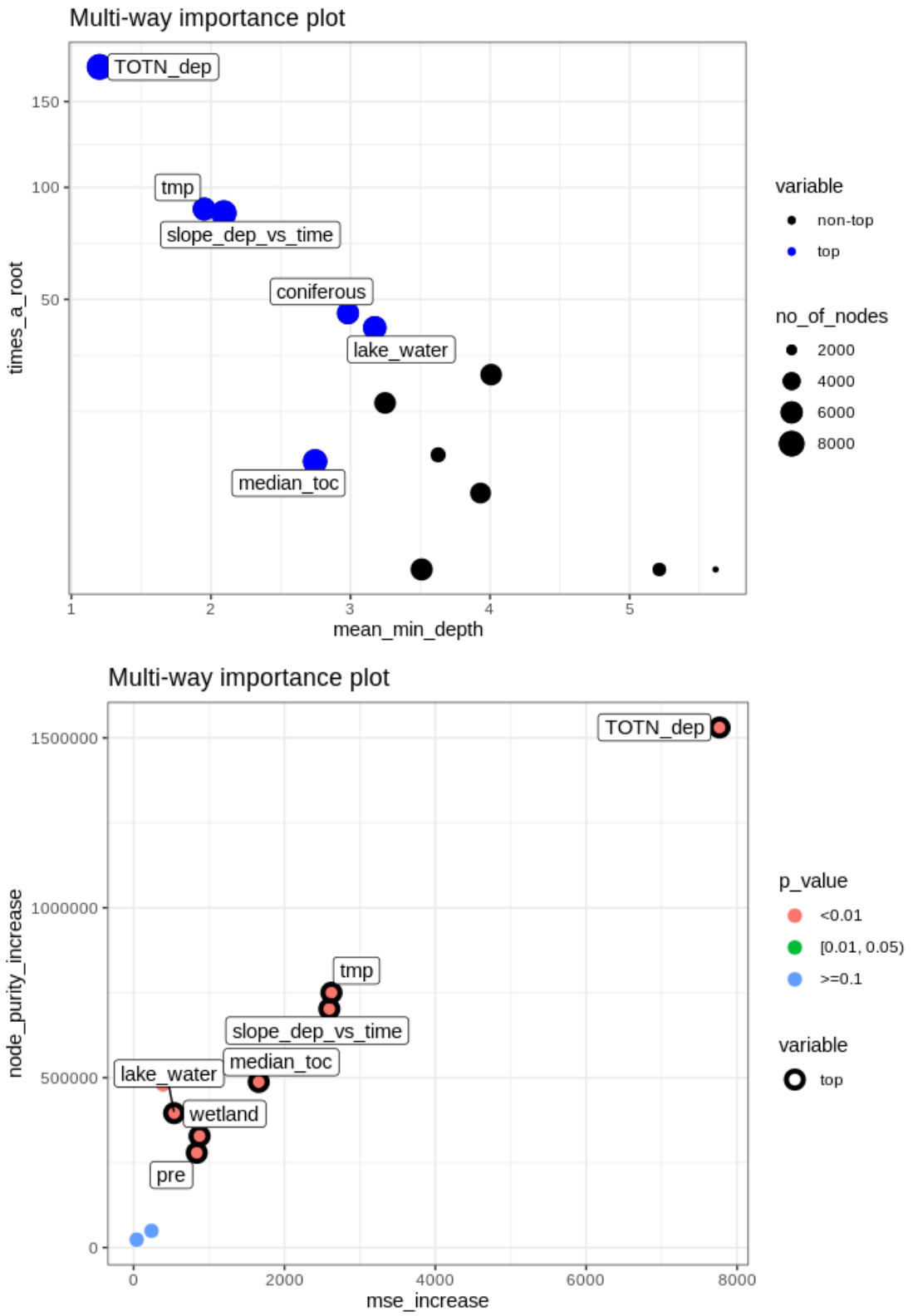

Figure 10. Multi-way importance plots showing the relative roles of variables in explaining the observed median 2012-2016 concentrations of NO_3 at ICP Waters sites. **Top**: times_a_root vs. mean_min_depth (most important variables to the upper left); **bottom**: node_purity _increase vs. mse_increase (most important variables to the upper right).

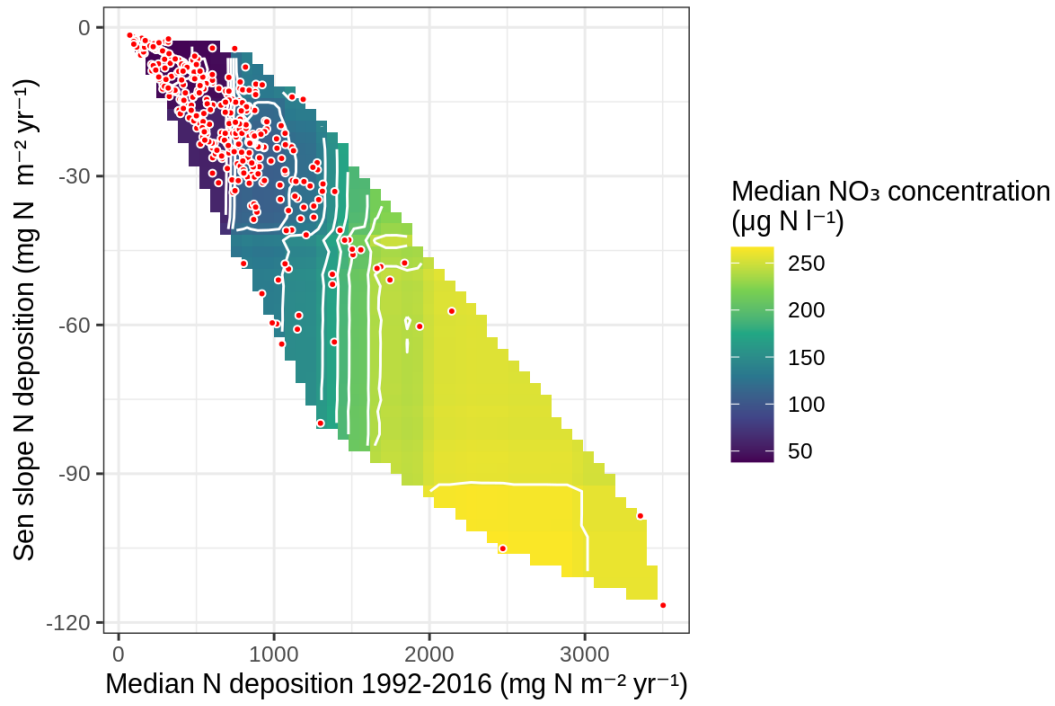

Figure 11. Predictor diagram for the variables **median N deposition 1992-2016** and **Sen slope N deposition 1992-2016**. The colours indicate the predicted median NO_3 concentration 2012-2016 for a given combination of predictor variable values. The red dots represent the ICP Waters sites included in the analysis.

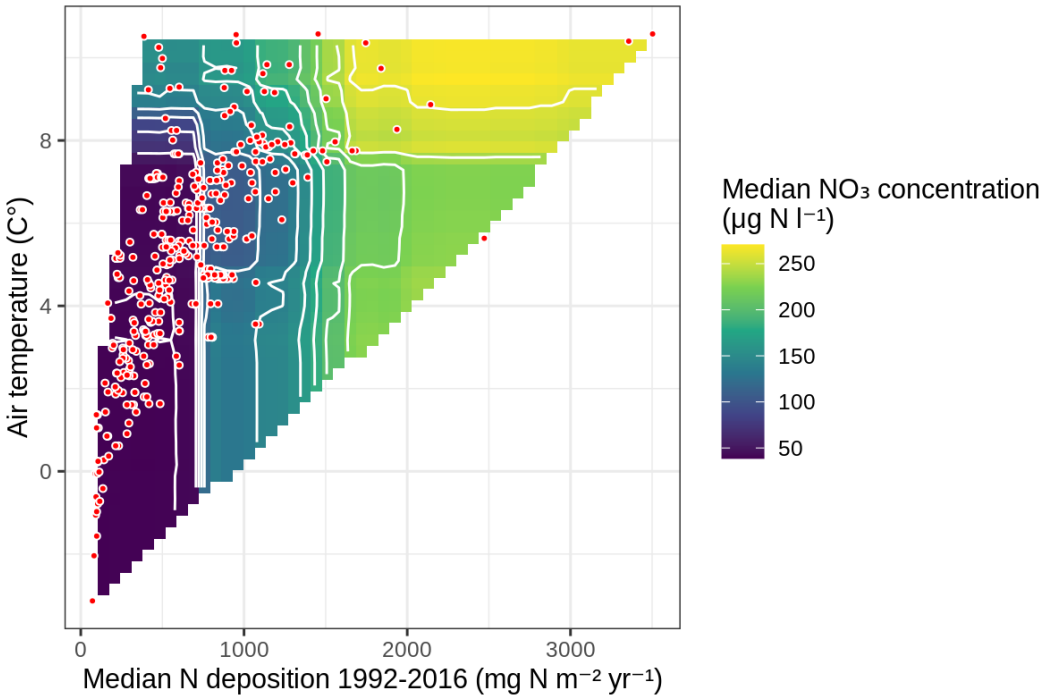

Figure 12. Predictor diagram for the variables **median N deposition 1992-2016** and **median air temperature 1992-2016**. The colours indicate the predicted median NO_3 concentration 2012-2016 for a given combination of predictor variable values. The red dots represent the ICP Waters sites included in the analysis.

3.1.3 Statistical analysis of NO_3 trends 1992-2016

We used the random forest analysis to explain the observed trends in NO_3 concentrations over the time period 1992-2016 at the ICP Waters sites. The explanatory variables included in the analysis are listed in **Table 2**.

Site selection

Catchment area was not included because this would decrease the number of sites available for the analysis substantially. Including TOC concentration reduced the number of sites somewhat (by 21), but this variable showed too high importance to be excluded. **Table 5** shows the number of sites included in or excluded from the analysis, based on availability of explanatory variables. Apart from the 21 sites lacking long-term (1992-2016) TOC concentration, some sites also lacked the forest sub-categories (cf. section 2.3.2).

Of the 423 sites selected for this analysis 199 had decreasing trends, 209 had no trend and only 15 had significant increases in NO_3 concentrations over time.

Table 5. Sites included in or excluded from the analysis, by country.

	Excluded	**Included**
Canada	3	103
Czech Republic	1	7
Finland	0	24
Germany	4	15
Ireland	3	0
Italy	5	0
Latvia	1	0
Netherlands	1	2
Norway	0	80
Poland	0	5
Slovakia	0	12
Sweden	6	81
Switzerland	6	0
United Kingdom	0	21
United States	0	73
Total	**30**	**423**

Results from random forest analysis

The explanatory variables are not fully independent of one another. The correlation matrix for the selected variables at the 423 sites shows that there are significant autocorrelations between several pairs of variables (**Figure 13**). Several of the correlations are central to the interpretation of the NO_3 trend data. Median 1992-2016 NO_3 concentrations are positively correlated with median 1992-2016 N deposition, and negatively correlated with the slope of deposition over time. The slope of deposition over time is negatively correlated with median N deposition. In other words, higher N deposition gives higher NO_3 concentrations, and the decreasing trends in N deposition are greater (more negative Sen slope) at sites with higher N deposition. N deposition is thus a key factor in explaining the general level of NO_3 concentrations. And the trend in N deposition over time is a key factor in explaining the decreasing trends in NO_3 concentrations (**Figure 14**).

Both of the multi-way importance plots in **Figure 14** (cf. section 2.3.2 for further explanation) indicate that four factors stand out as key in explaining whether NO_3 concentrations at ICP Waters sites have declined significantly: the median NO_3 concentration, N deposition (median and slope), percentage of coniferous forest, and median TOC.

The median NO_3 concentration turns out to be the main factor for NO_3 trends at the ICP Waters sites. Sites with the highest median NO_3 concentration levels also have the strongest downward NO_3 trends (**Figure 15**). There is a tendency towards stronger downward NO_3 trends at sites with very high percentages of coniferous forest in the catchment, but median NO_3 concentration seems to be a much stronger explanatory variable than coniferous forest coverage.

Both the median N deposition level and the slope of N deposition over time are strong explaining variables for the NO_3 trend (**Figure 16**). The strongest decreasing NO_3 trends are found at sites with median N deposition above about 800 mg N m^{-2} yr^{-1}, and at sites where N deposition has decreased more than 40-50 mg N m^{-2} yr^{-1} during the last 25 years (Sen slope, 1992-2016).

The ICP Waters data show a clear pattern of "antagonism" between TOC and NO_3 concentrations: most sites with high TOC have low NO_3 whereas most sites with high NO_3 have low-intermediate TOC (**Figure 17**). The random forest analysis indicates that declines in NO_3 are especially likely at sites with very low TOC concentrations.

As there usually is a positive relationship between TOC level and percentage of coniferous forest in the catchment (cf. **Figure 13**), it is an apparent contradiction that the analysis indicates a somewhat higher probabilty for downward NO_3 trends at sites with very high percentages of coniferous forest in the catchment (**Figure 15**). However, the relationship is relatively weak, and it is possible that also other factors can be responsible for declining NO_3 trends in the few catchments that are fully forested with conifers.

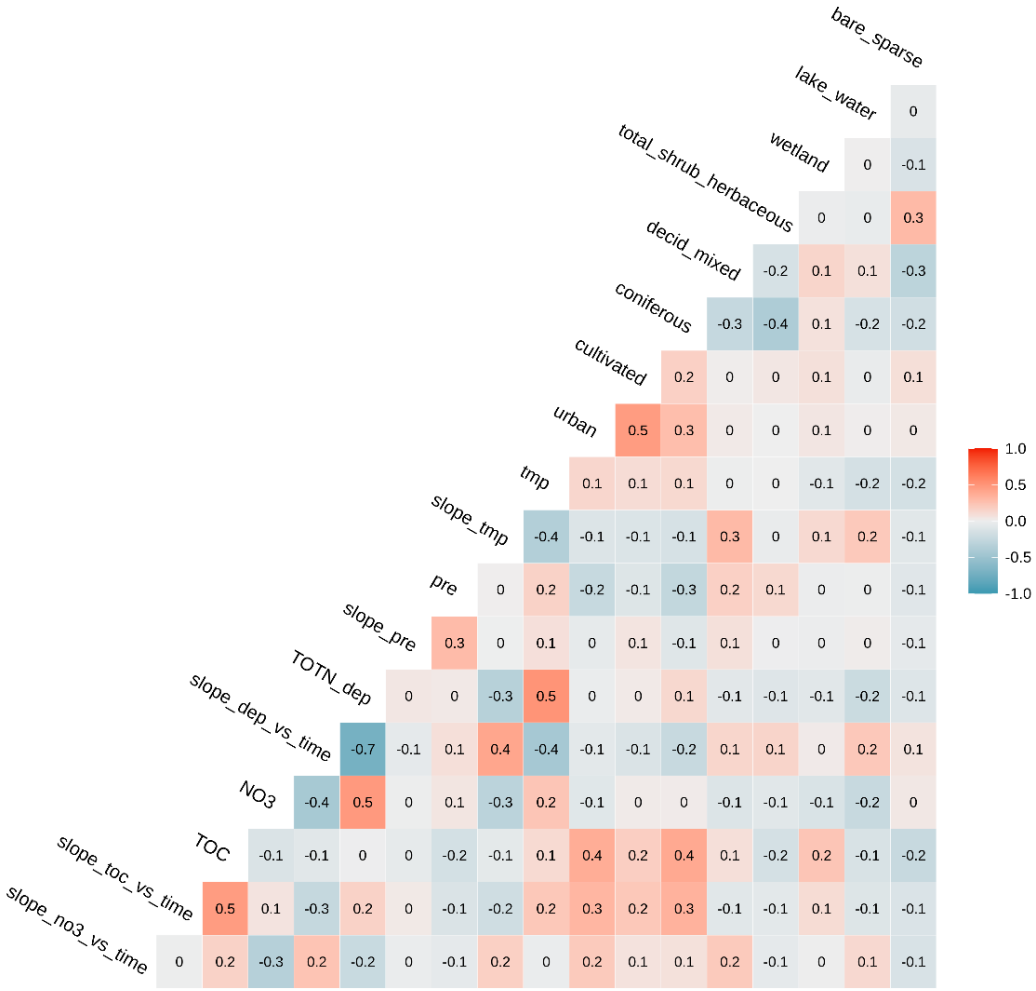

Figure 13. Correlation matrix for the explanatory variables and the response variable (slope_no3_vs_time) used in the analysis of NO_3 trends at 423 ICP Waters sites (cf. **Table 2** for explanatory variable names).

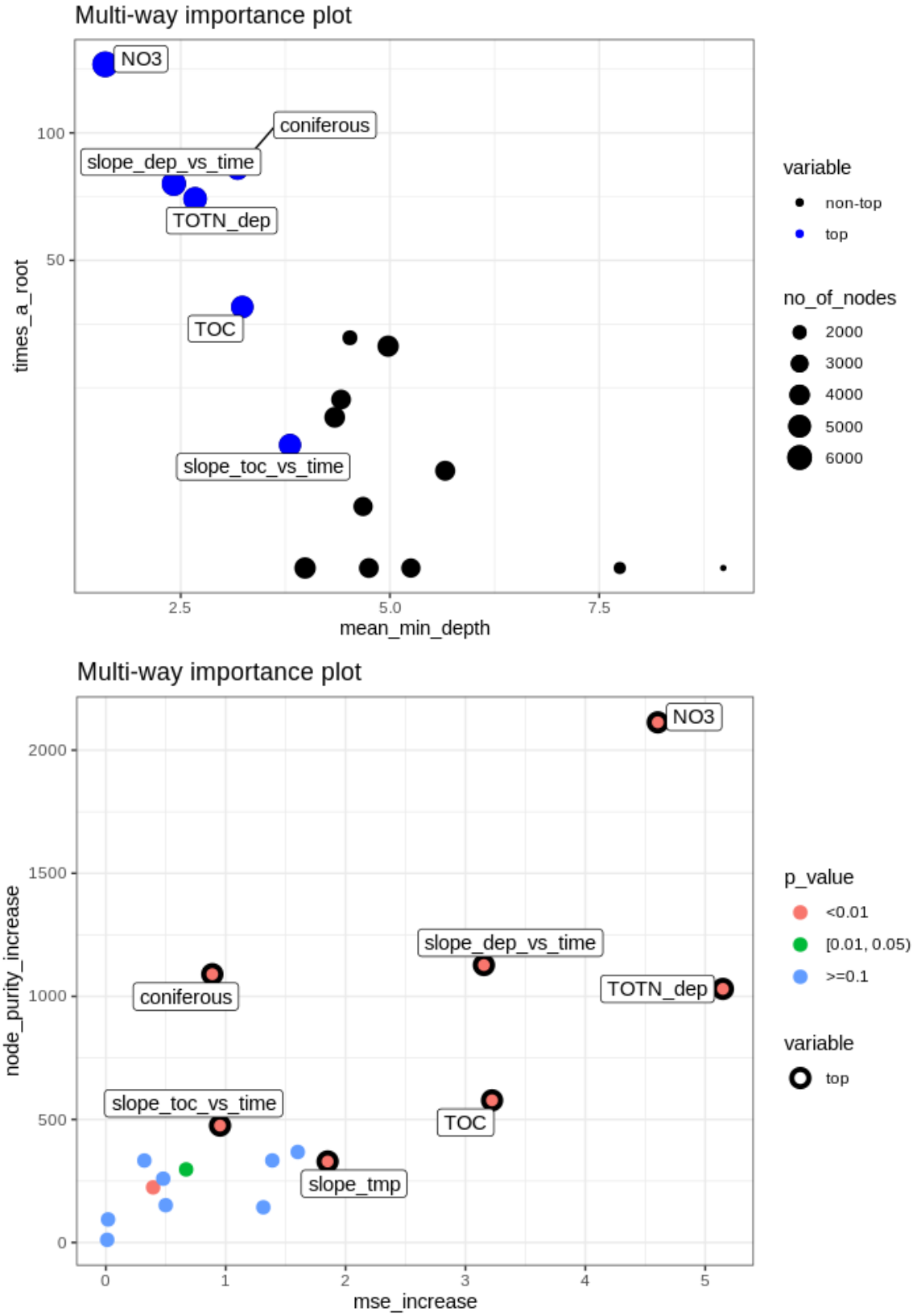

Figure 14. Multi-way importance plots showing the relative roles of variables in explaining the observed time trends 1992-2016 in NO_3 concentrations at ICP Waters sites. **Top**: times_a_root vs. mean_min_depth (most important variables to the upper left); **bottom**: node_purity _increase vs. mse_increase (most important variables to the upper right).

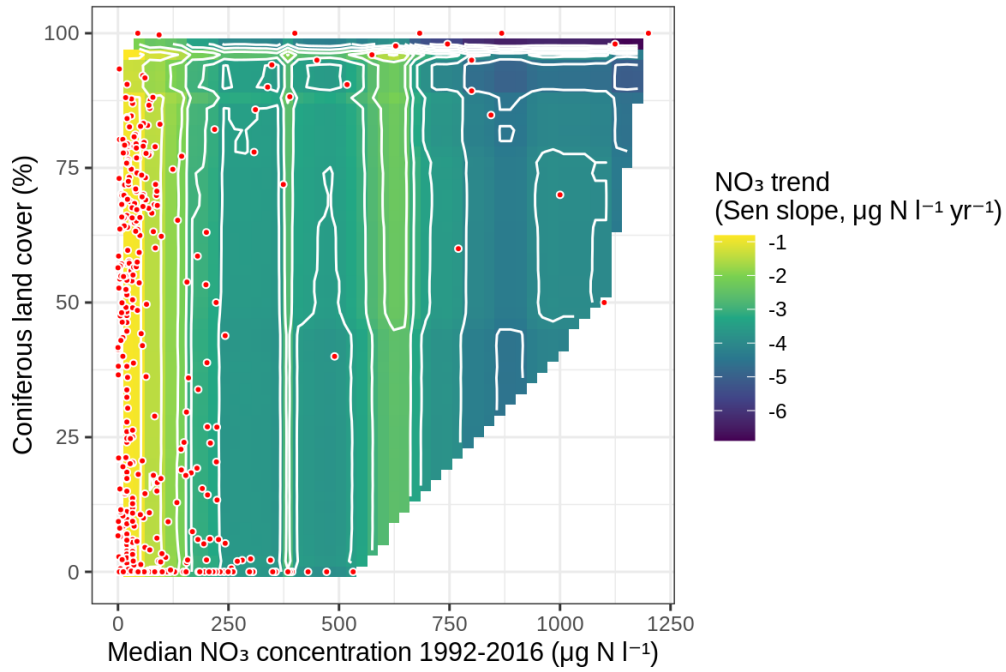

Figure 15. Predictor diagram for the variables **median NO_3 concentration 1992-2016** and **percentage coniferous forest in the catchment**. The colours indicate expected trend in NO_3 (Sen slope, 1992-2016) for a given combination of predictor variable values. The red dots represent the ICP Waters sites included in the analysis.

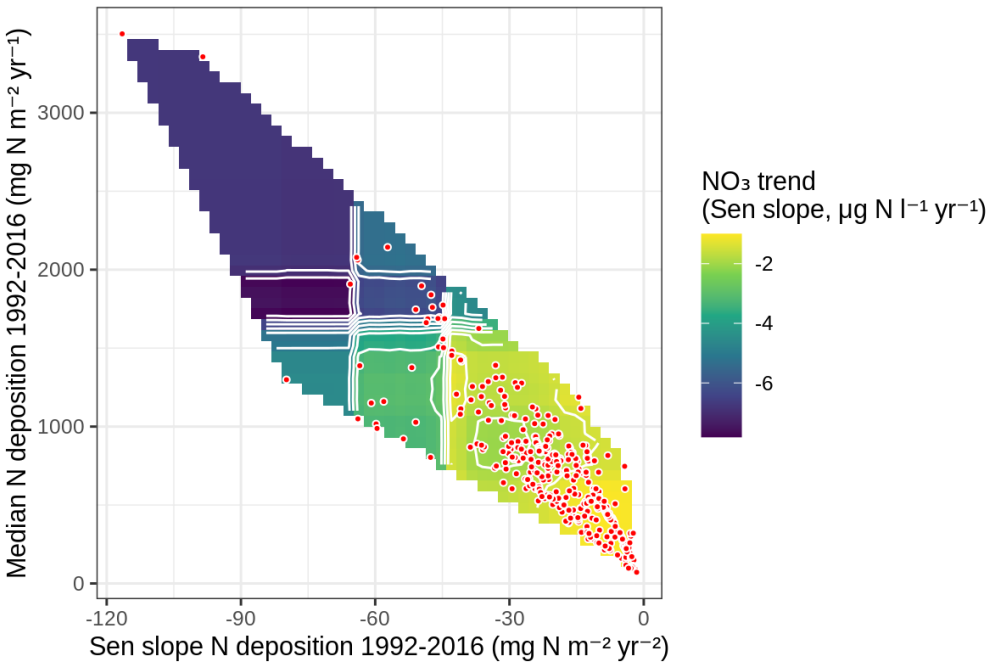

Figure 16. Predictor diagram for the variables **Sen slope N deposition 1992-2016** and **median N deposition 1992-2016**. The colours indicate expected trend in NO_3 (Sen slope, 1992-2016) for a given combination of predictor variable values. The red dots represent the ICP Waters sites included in the analysis.

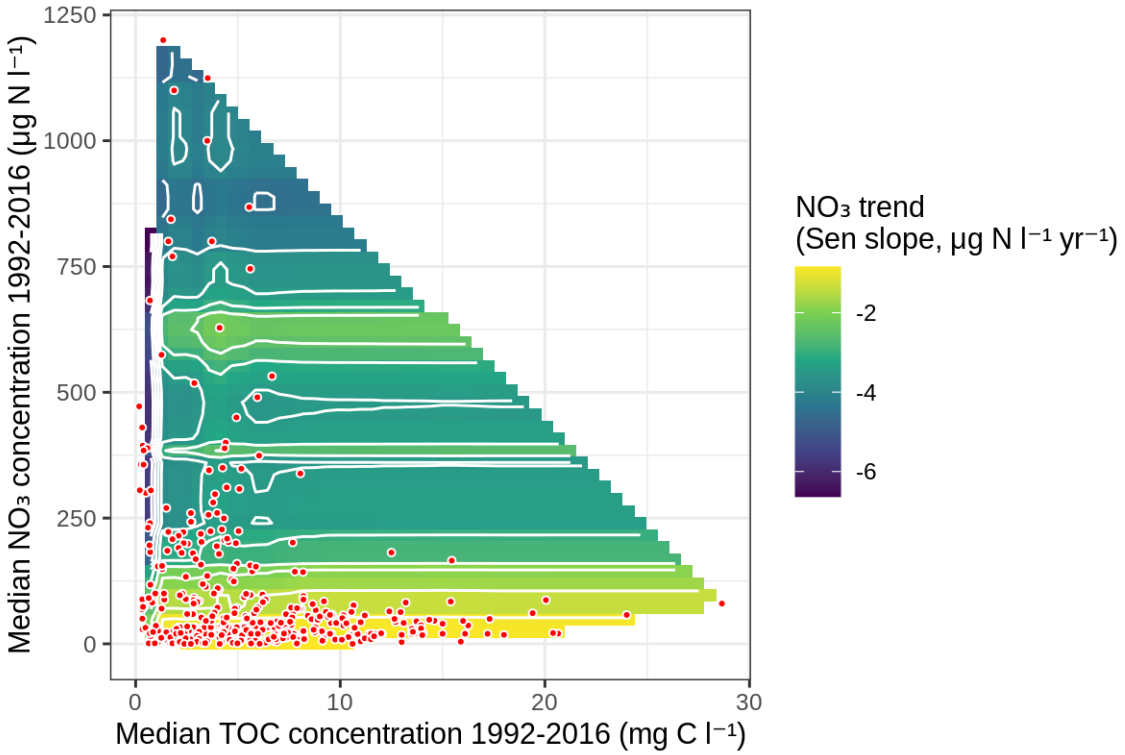

Figure 17. Predictor diagram for the variables **median TOC concentration 1992-2016** and **median NO_3 concentration 1992-2016**. The colours indicate expected trend in NO_3 (Sen slope, 1992-2016) for a given combination of predictor variable values. The red dots represent the ICP Waters sites included in the analysis.

3.2 TOC/TON

3.2.1 Data overview

Median TOC/TON

There were far fewer ICP Waters sites with valid median TOC/TON (288) than median NO_3 concentration (446) for 2012-2016, reducing the number of countries included in the TOC/TON analysis (**Figure 18**).

Median TOC/TON ranged from 4 to 59 with a median of 26. The highest values were found in Nova Scotia in Canada, in eastern Norway/western Sweden and in the UK, in addition to single sites in Finland and the Czech Republic. The lowest TOC/TON was observed in Ontario, coastal, mountainous and northern Norway, southeastern Finland, southern Sweden and in Germany and Italy.

The median TOC/TON was positively related to the median TOC concentration, and to a lesser extent also the median TON concentration (**Figure 19**). At higher TOC/TON the range in TOC and TON concentrations is larger.

TOC/TON trend

Of the 214 sites with valid TOC/TON trend, only 10 sites had significantly decreasing TOC/TON: Six in Norway, three in Canada and one in Germany (**Figure 20**). More than 50% of the sites (111) had significantly increasing trend in TOC/TON, while most of the remaining sites (93) had no significant trend.

There was no indication that the TOC/TON trend was related to the N deposition level (**Figure 21**). There was a tendency of higher Sen slopes for TOC/TON at higher TOC/TON levels for sites with significantly increasing TOC/TON (**Figure 22**).

There was a positive Sen slope for TOC at nearly all sites while the Sen slope for TON could be both positive and negative (**Figure 23**). A significant increase in TOC/TON was found where TOC increased to a larger extent than TON or where TON decreased. A significant decrease in TOC/TON was observed for sites with positive Sen slope in TON and small changes in TOC. The trend in TON showed no relationship with N deposition (**Figure 24**)

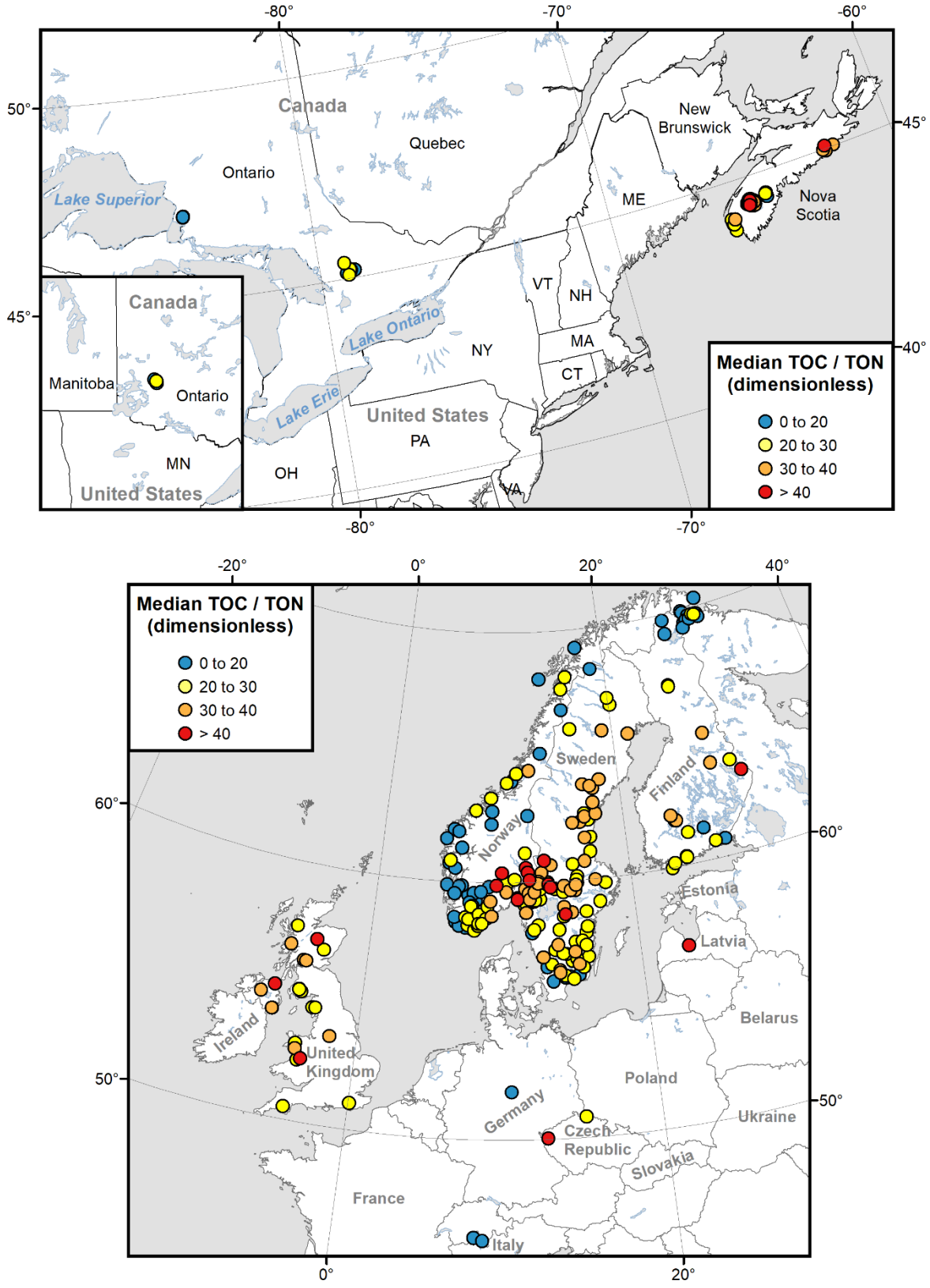

Figure 18. Map of median TOC/TON 2012-2016 at 288 sites with valid median.

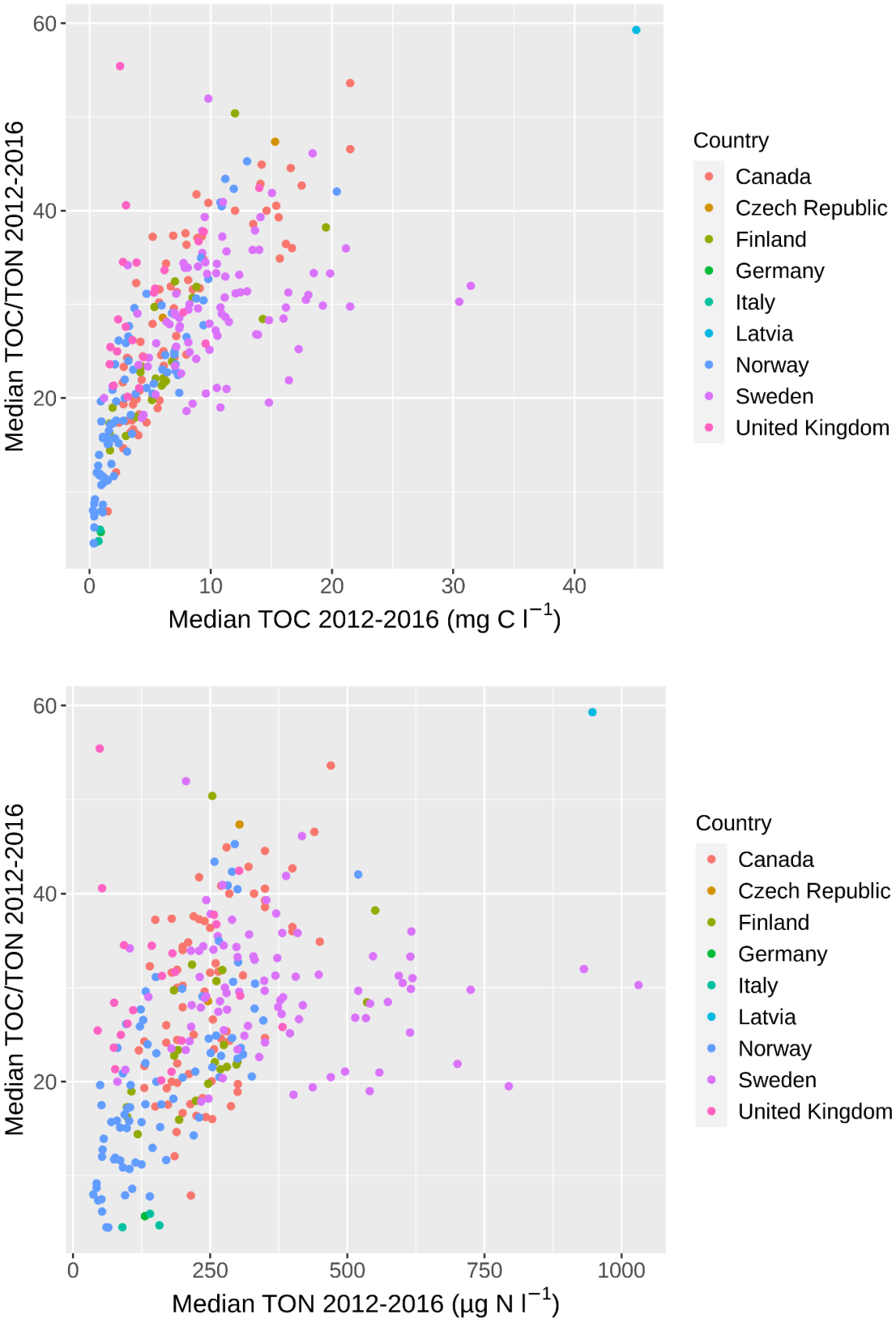

Figure 19. Median TOC/TON vs median TOC (top) and TON (bottom) 2012-2016 at the 288 sites with valid median TOC/TON.

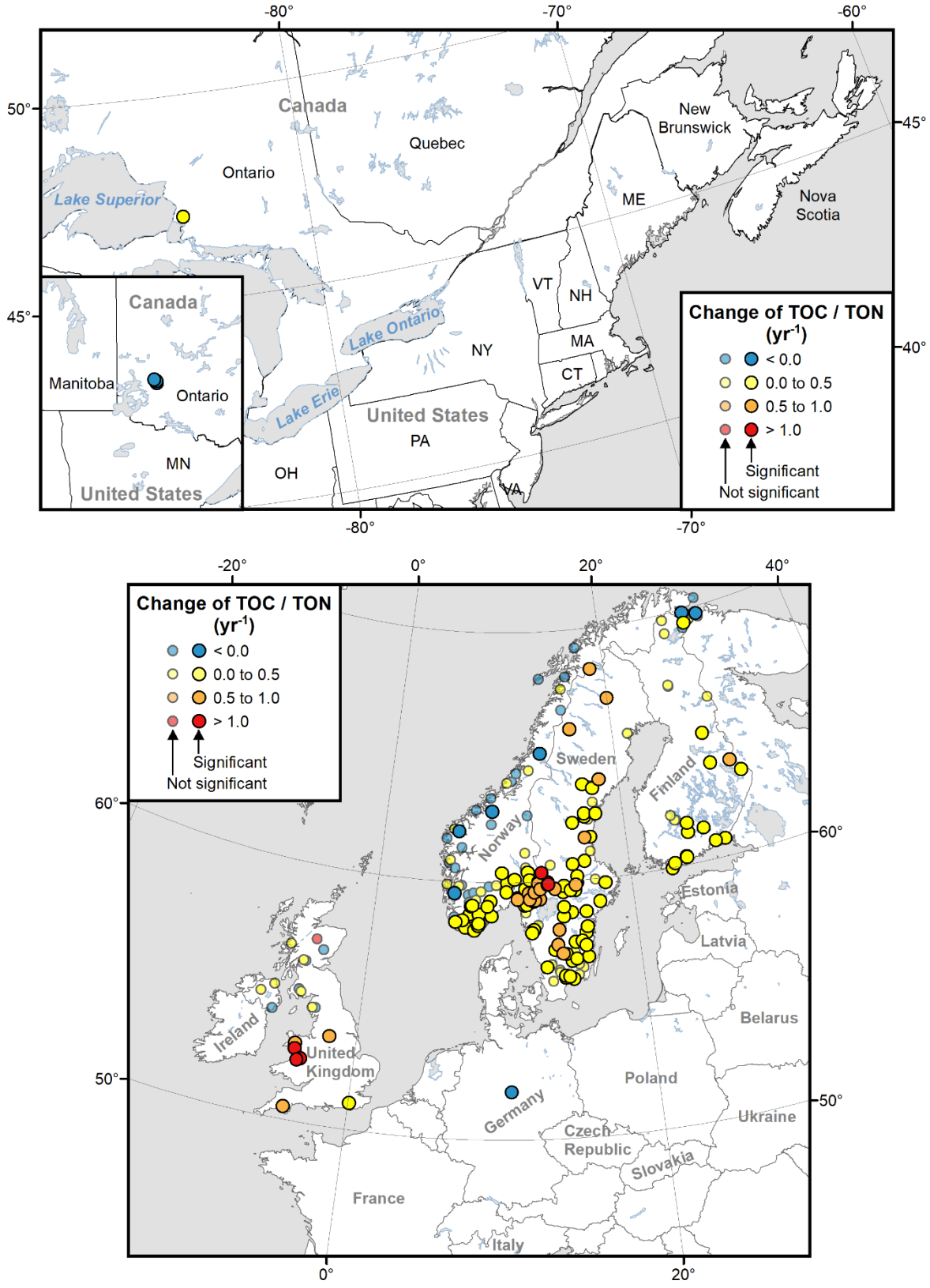

Figure 20. Map of trend in TOC/TON 1992-2016 at the 214 sites with valid trend.

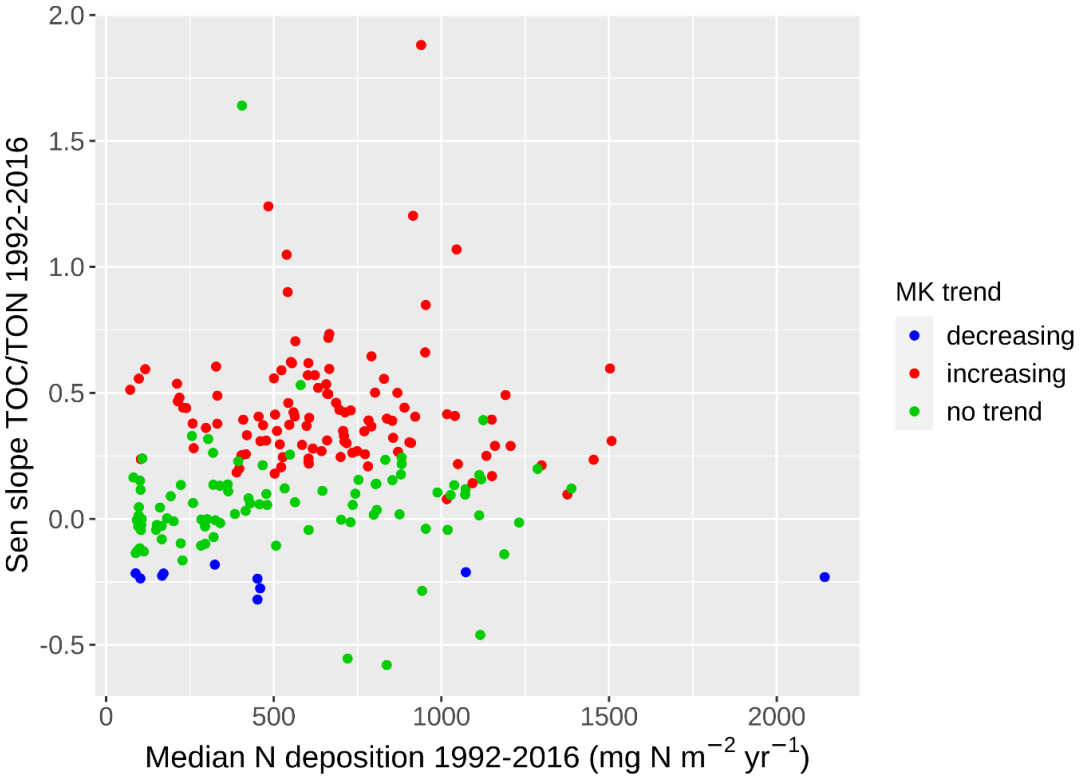

Figure 21. TOC/TON trend vs median N deposition 1992-2016. The colour indicates the significance level of the Mann-Kendall trend test at the 214 sites with valid TOC/TON trend.

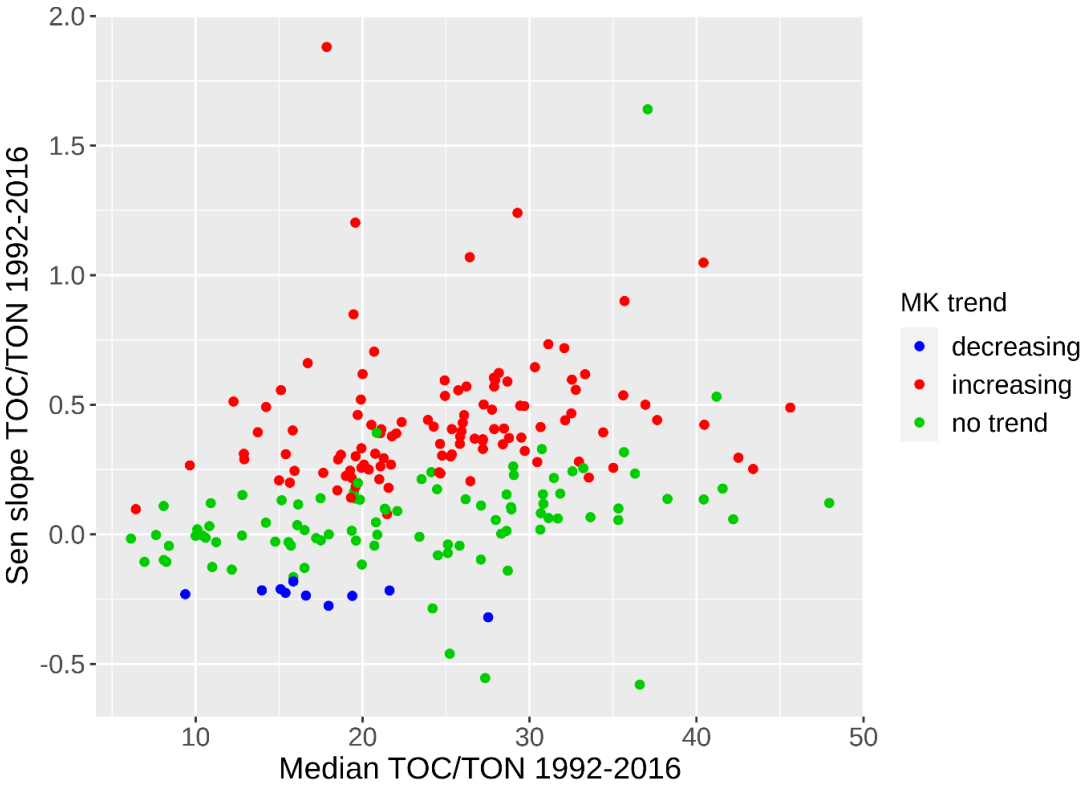

Figure 22. TOC/TON trend vs median TOC/TON 1992-2016. The colour indicates the significance level of the Mann-Kendall trend test at the 214 sites with valid TOC/TON trend.

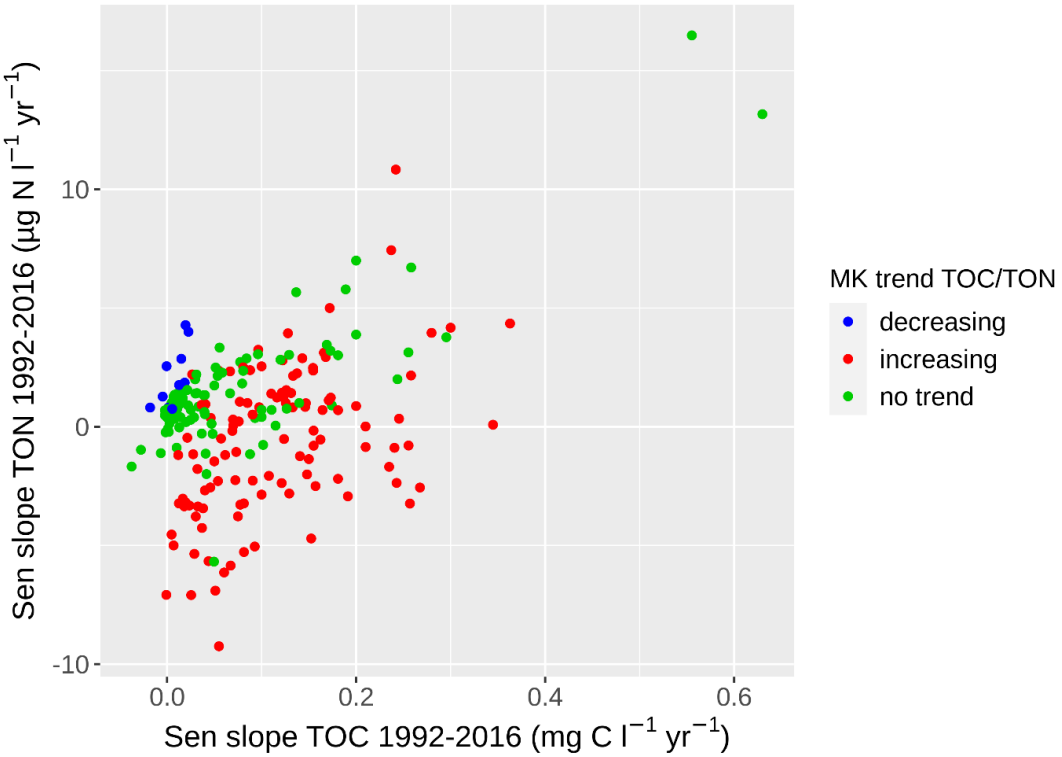

Figure 23. TON trend vs TOC trend 1992-2016. The colour indicates the significance level of the Mann-Kendall trend test for TOC/TON at the 214 sites with valid TOC/TON trend.

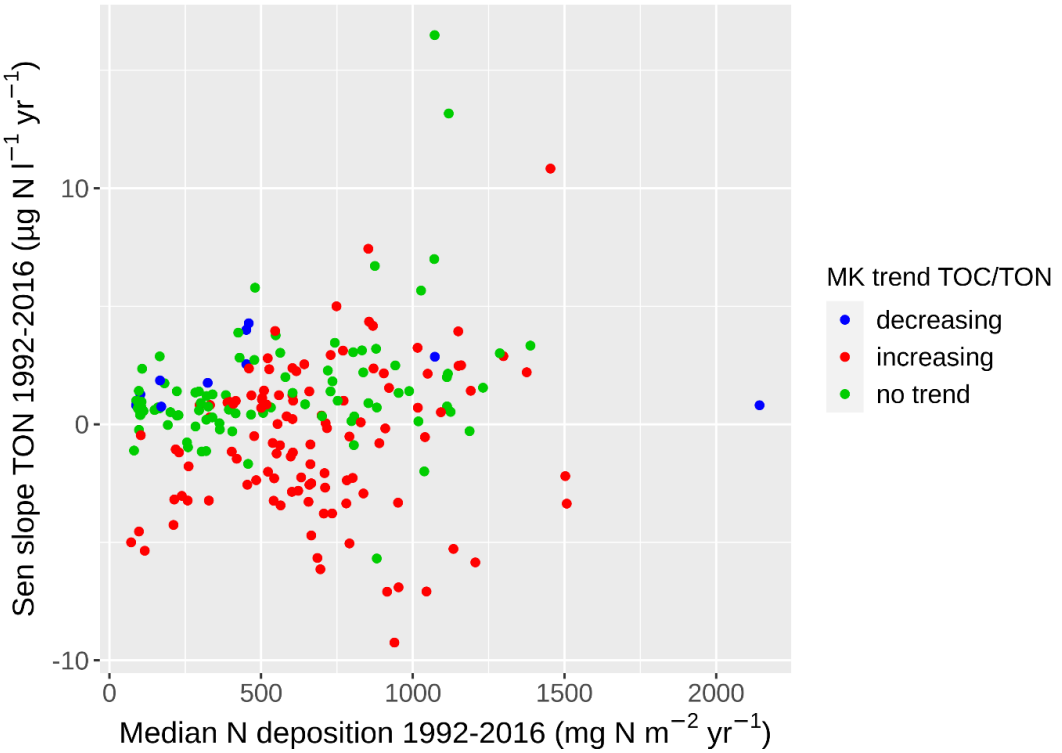

Figure 24. TON trend vs median N deposition 1992-2016. The colour indicates the significance level of the Mann-Kendall trend test for TOC/TON at the 214 sites with valid TOC/TON trend.

3.2.2 Spatial variability of TOC/TON median concentration ratios 2012-2016

The random forest analysis aims to explain the observed present-day geographic distribution of median TOC/TON concentration ratios 2012-2016 at the ICP Waters sites. The explanatory variables included in the analysis are listed in **Table 2**.

Site selection

All the sites with valid TOC/TON have catchment area, so in this analysis catchment area could be used. 285 of the 288 ICP Waters with TOC and TON data could be included (**Table 6**). The three excluded Canadian sites do not have forest cover split into sub-categories (coniferous and deciduous).

Table 6. Sites included in or excluded from the analysis, by country.

	Excluded	**Included**
Canada	3	67
Czech Republic	0	2
Finland	0	22
Germany	0	1
Italy	0	3
Latvia	0	1
Norway	0	80
Sweden	0	87
United Kingdom	0	22
Total	**3**	**285**

Results from random forest analysis

The correlation matrix for the selected variables shows that there are significant correlations between several pairs of variables (**Figure 25**). TOC and TON are strongly correlated; thus they behave similarly relative to the other variables. TOC and TON concentrations show a strong positive relationship with the cover of coniferous forest and urban areas in the catchment, while there is a negative relationship with shrub/herbaceous and bare/sparsely vegetated land.

The multi-way importance diagrams indicate that the median TOC concentration is the dominant factor explaining the median TOC/TON ratios at the ICP Waters sites (**Figure 26**). Median TON concentration comes in a weak second place. Both of these, of course, are part of the TOC/TON ratio, and are not independent factors. None of the catchment characteristics appear to play a substantial role.

TOC/TON is predicted to be higher for sites with high TOC concentration (**Figure 27**). Hence, TOC concentration appears to be the determining variable for TOC/TON ratios, while TON follows more passively given the strong positive correlation between TON and TOC.

A similar plot for coniferous forest and lake/water shows that these variables are important for some sites (**Figure 28**). The prediction shows that TOC/TON is lower at increasing percentages of lakes and open water in the catchment.

The role of coniferous forest is more unclear from **Figure 28**, but in a parallel analysis excluding TOC and TON concentration as explanatory variables, the share of coniferous forest appears as the most important variable. This fits well with the positive correlation between TOC and TON and coniferous forest cover. The relationship between TOC/TON, TOC concentration and forest cover is also shown in **Figure 29**. At low TOC/TON the sites generally have low coniferous forest cover. At higher TOC/TON, the sites with high coniferous forest cover frequently have higher TOC (and consequently TON). At sites with low forest cover, TOC/TON can also be related to vegetation types with different C/N ratios in their soils; e.g., heathlands.

Median N deposition and N deposition trend do not appear as important explanatory variables for median TOC/TON concentration ratio in the multi-way importance plots (**Figure 26**). However, the two-way plot in **Figure 30** indicates a negative relationship between median TOC/TON ratios and N deposition level and trend.

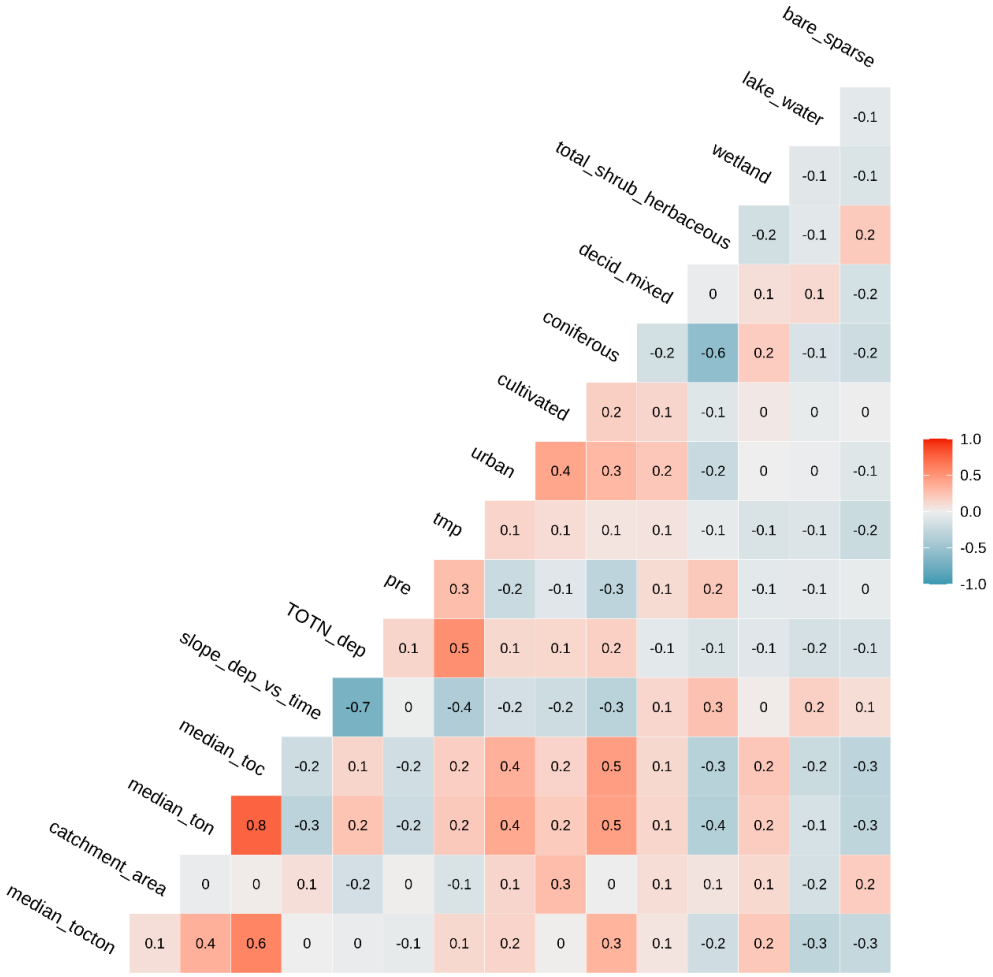

Figure 25. Correlation matrix for the explanatory variables and the response variable (median_tocton) used in the analysis of median TOC/TON 2012-2016 at 285 ICP Waters sites (cf. **Table 2** for explanatory variable names).

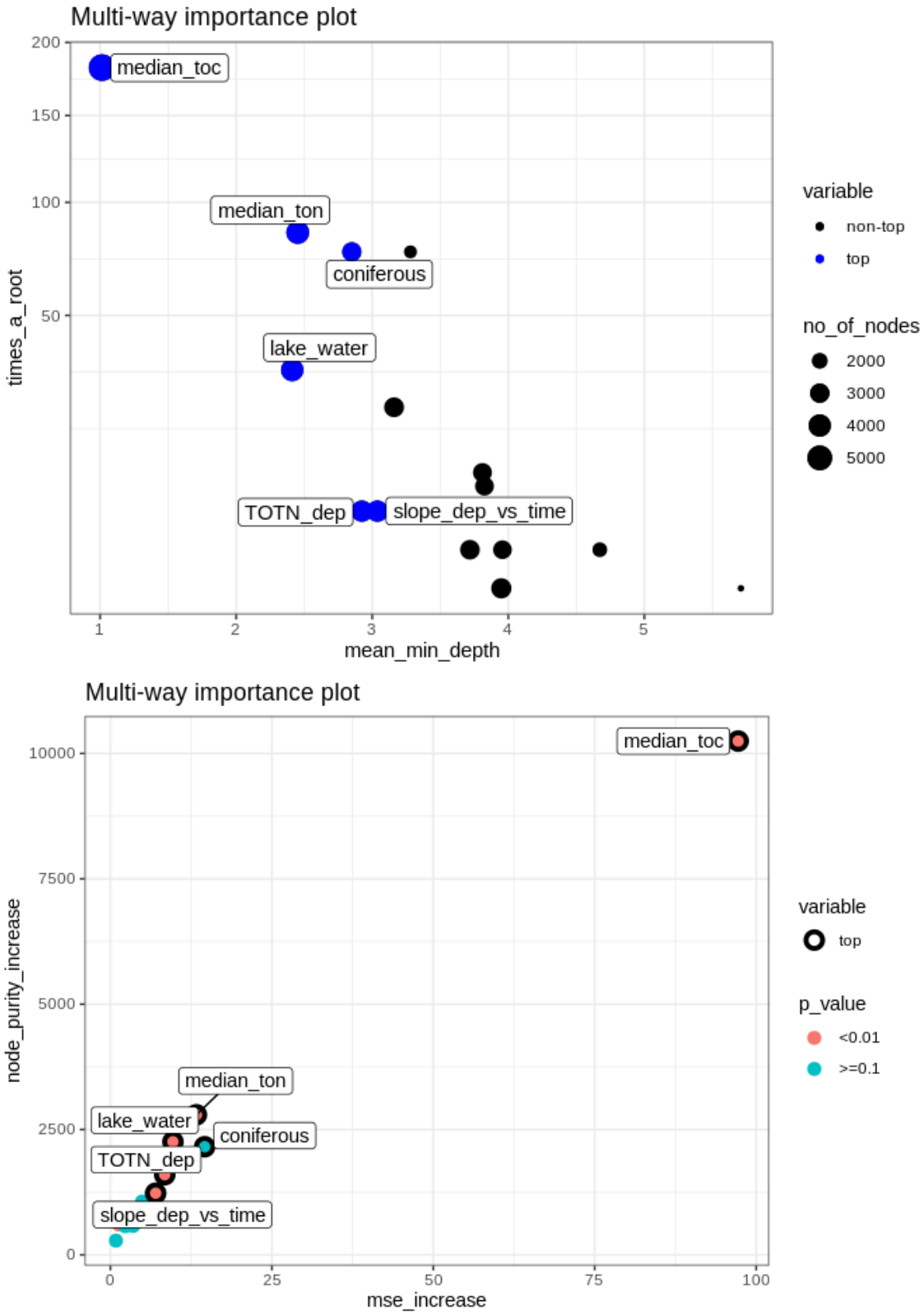

Figure 26. Multi-way importance plots showing the relative roles of variables in explaining the observed median 2012-2016 TOC/TON concentration ratios at ICP Waters sites. **Top**: times_a_root vs. mean_min_depth (most important variables to the upper left); **bottom**: node_purity _increase vs. mse_increase (most important variables to the upper right).

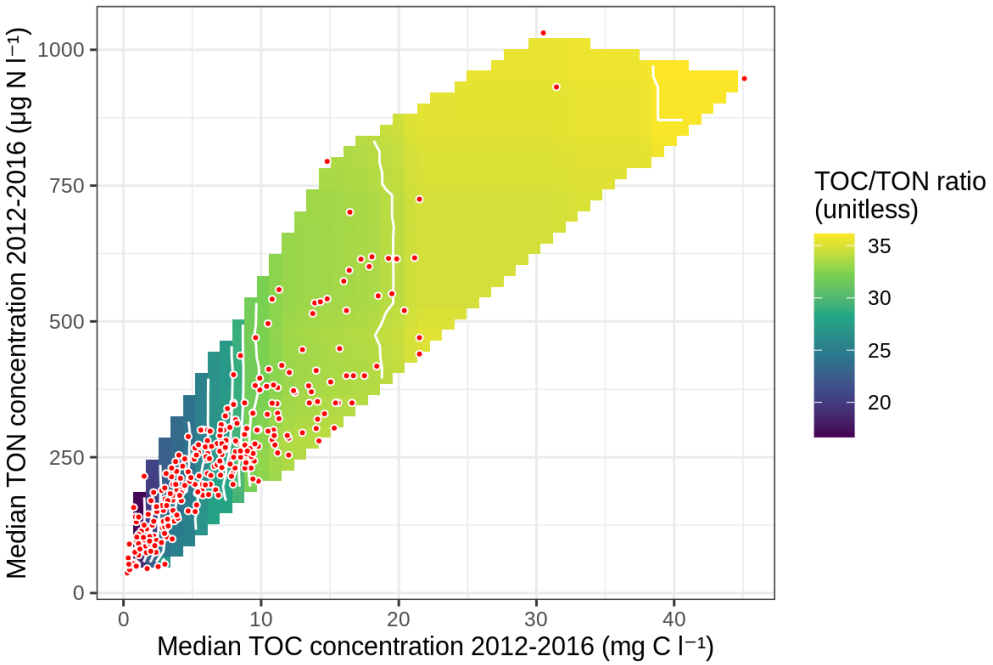

Figure 27. Predictor diagram for the variables **median TOC concentration 2012-2016** and **median TON concentration 2012-2016**. The colours indicate the predicted median TOC/TON ratio 2012-2016 for a given combination of predictor variable values. The red dots represent the ICP Waters sites included in the analysis.

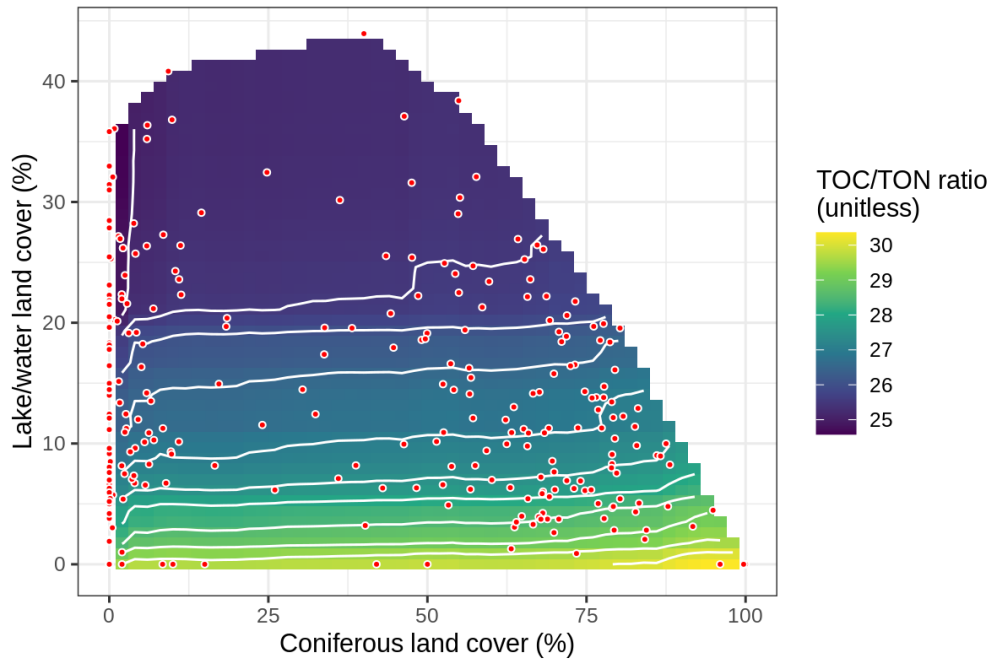

Figure 28. Predictor diagram for the variables **percentage coniferous forest in catchment** and **percentage lake/water in the catchment**. The colours indicate the predicted median TOC/TON ratio 2012-2016 for a given combination of predictor variable values. The red dots represent the ICP Waters sites included in the analysis.

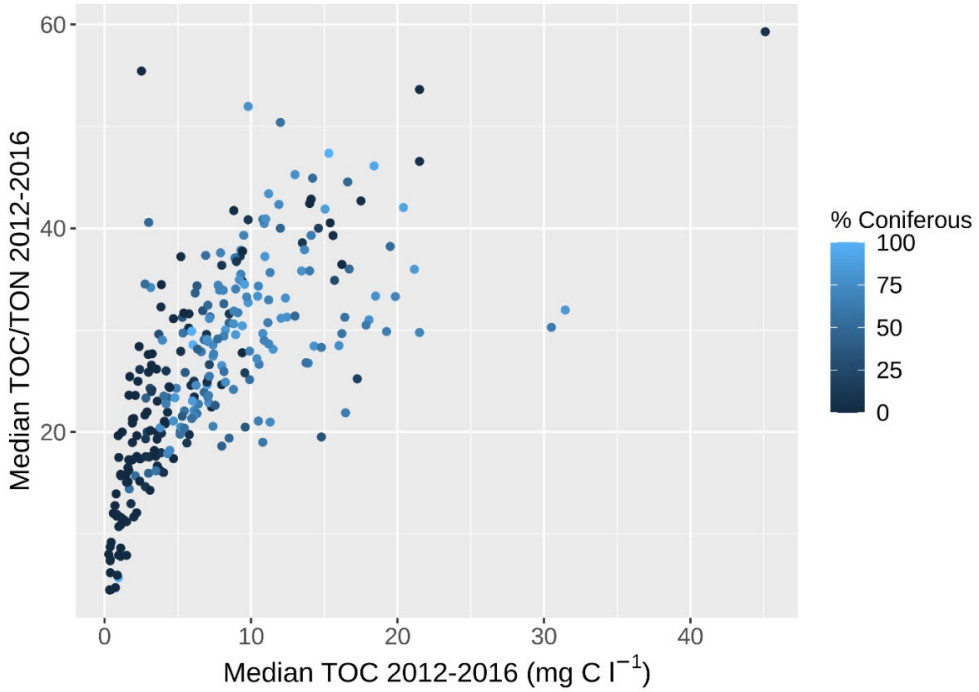

Figure 29. Median TOC/TON vs median TOC (top) or TON (bottom) 2012-2016 at the 285 sites with valid median TOC/TON and all explanatory variables. The colour reflects the percentage cover of coniferous forest.

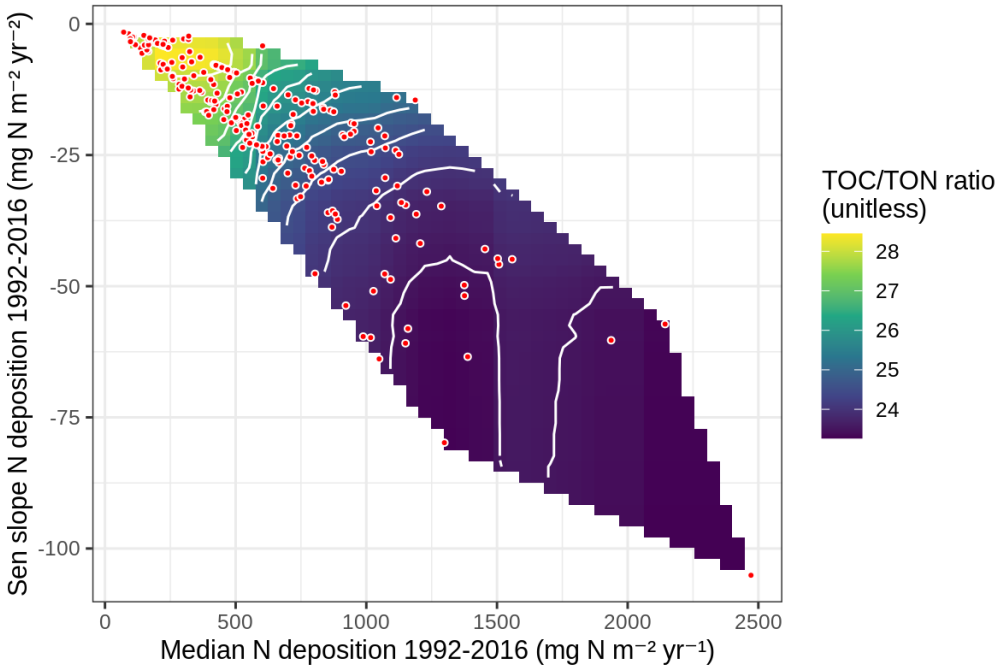

Figure 30. Predictor diagram for the variables **median N deposition 1992-2016** and **Sen slope N deposition 1992-2016**. The colours indicate the predicted median TOC/TON ratio 2012-2016 for a given combination of predictor variable values. The red dots represent the ICP Waters sites included in the analysis.

3.2.3 Statistical analysis of TOC/TON trends 1992-2016

We used random forest analysis to help explaining the observed trends in TOC/TON concentration ratios over the time period 1992-2016 at the ICP Waters sites. The explanatory variables included in the analysis are listed in **Table 2**.

Site selection

Of the 288 ICP Waters with TOC and TON data, 211 had long-term records for both variables. Like for median TOC/TON, catchment area could be included as explanatory variable. The sites included or excluded from the analysis are listed by country in **Table 7**. Again, three Canadian sites were excluded as they do not have forest cover split into sub-categories.

Table 7. Sites included in or excluded from the analysis, by country.

	Excluded	Included
Canada	3	4
Finland	0	24
Germany	0	1
Norway	0	80
Sweden	0	81
United Kingdom	0	21
Total	**3**	**211**

Results from random forest analysis

The explanatory variables are not fully independent of one another. The correlation matrix for the selected variables at the 211 sites shows that there are significant correlations between several pairs of variables (**Figure 31**).

Both of the multi-way importance plots in **Figure 32** indicate the following factors stand out as key in explaining TOC/TON concentration ratios at the ICP Waters sites: trend in TON over time, percentage coniferous forest, trend in TOC over time, and median TOC and TON concentrations.

As could be expected, there is a high degree of intercorrelation between medians and trends of TON and TOC concentrations (cf. **Figure 31**). Nearly all the sites have positive Sen slopes for TOC and TOC/TON concentration ratios, whereas Sen slopes for TON are more evenly distributed on the positive and negative side (**Figure 33**, **Figure 34**). Not surprisingly, the probability of increasing TOC/TON trends is highest at sites with high and increasing TOC concentrations, whereas increasing TON trends points in the opposite direction. Sites with a high percentage of coniferous forest show a higher probability of increasing TOC/TON trends, which also could be expected as coniferous forest is positively correlated with both median level and trend for TOC and TON (**Figure 31**).

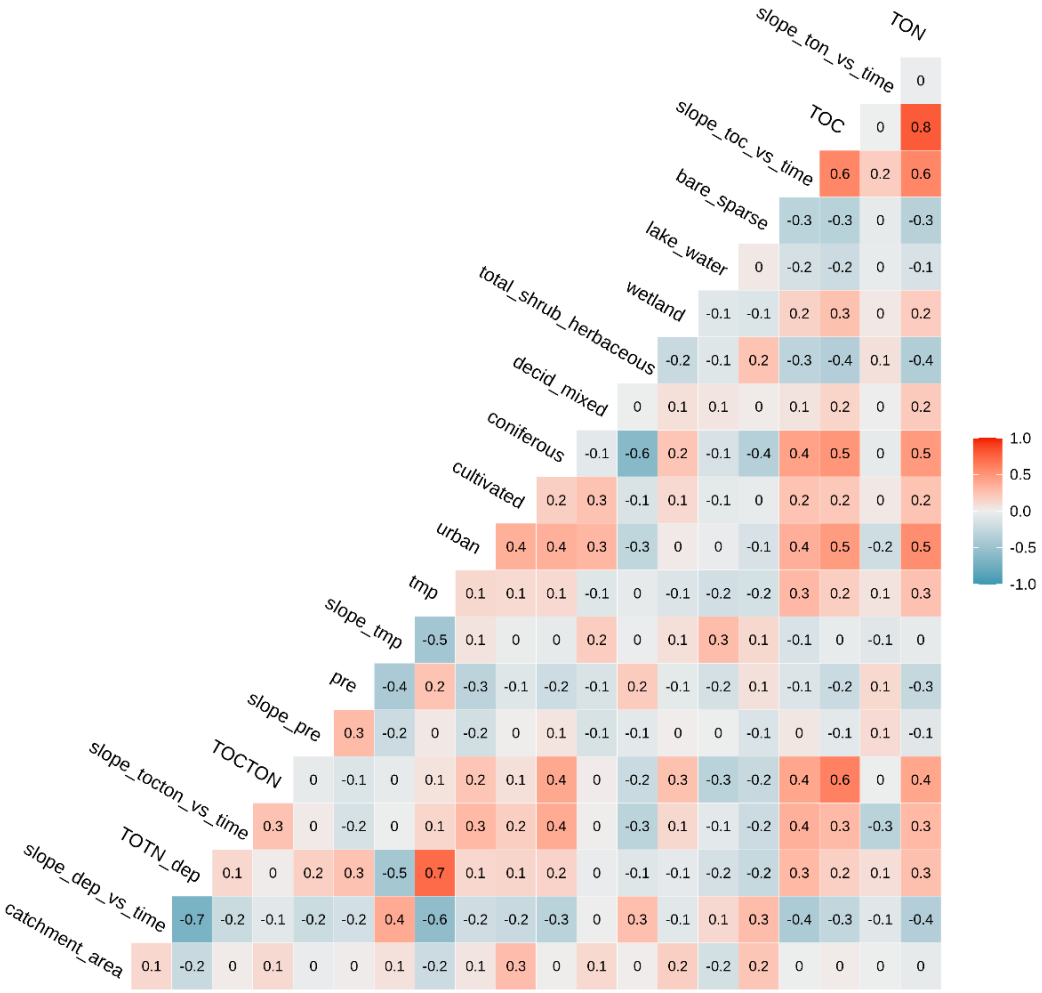

Figure 31. Correlation matrix for the explanatory variables and the response variable (slope_tocton_vs_time) used in the analysis of TOC/TON trends at 423 sites ICP Waters sites (cf. **Table 2** for explanatory variable names).

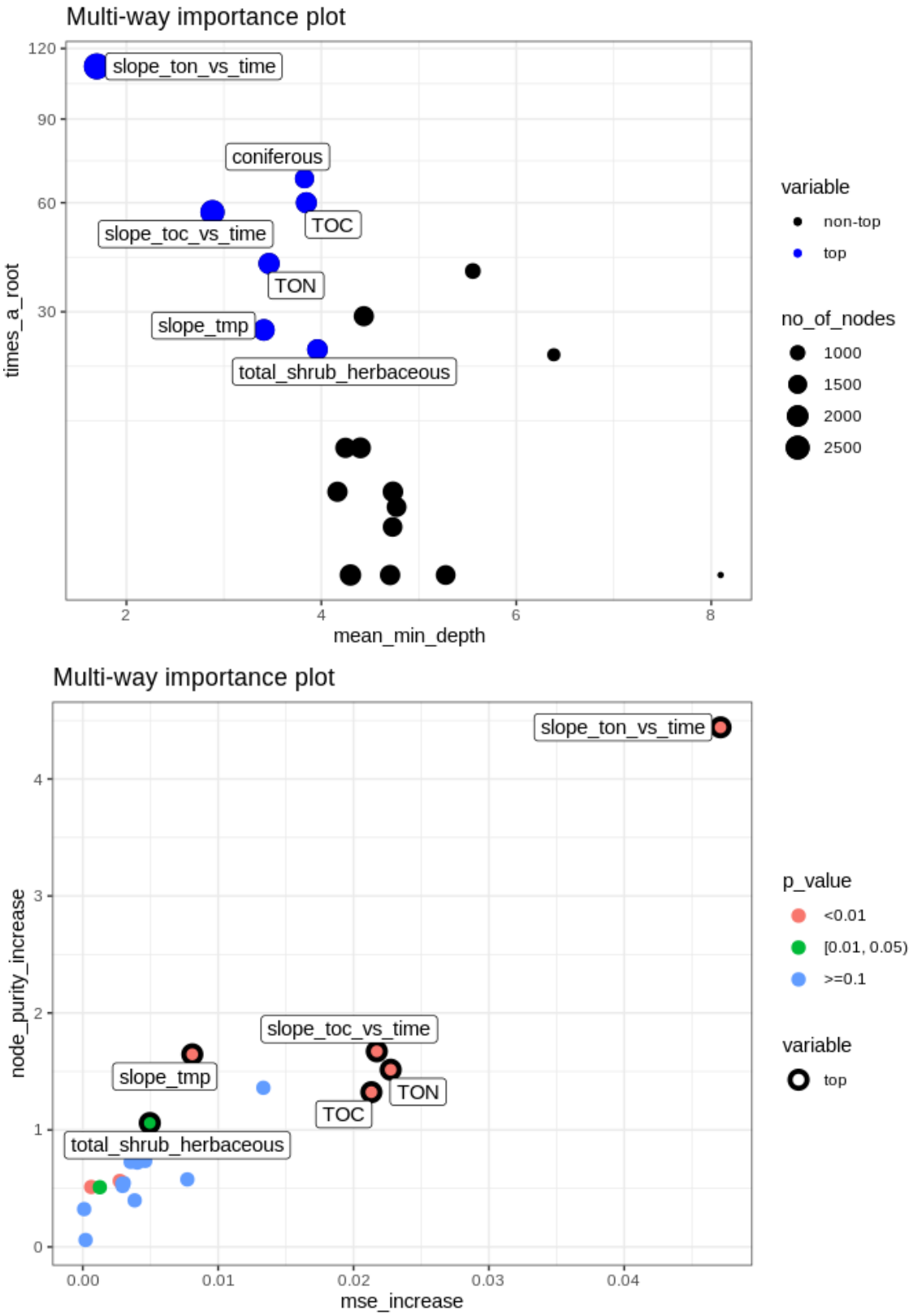

Figure 32. Multi-way importance plots showing the relative roles of variables in explaining the observed time trends 1992-2016 in TOC/TON concentration ratios at ICP Waters sites. **Top**: times_a_root vs. mean_min_depth (most important variables to the upper left); **bottom**: node_purity _increase vs. mse_increase (most important variables to the upper right).

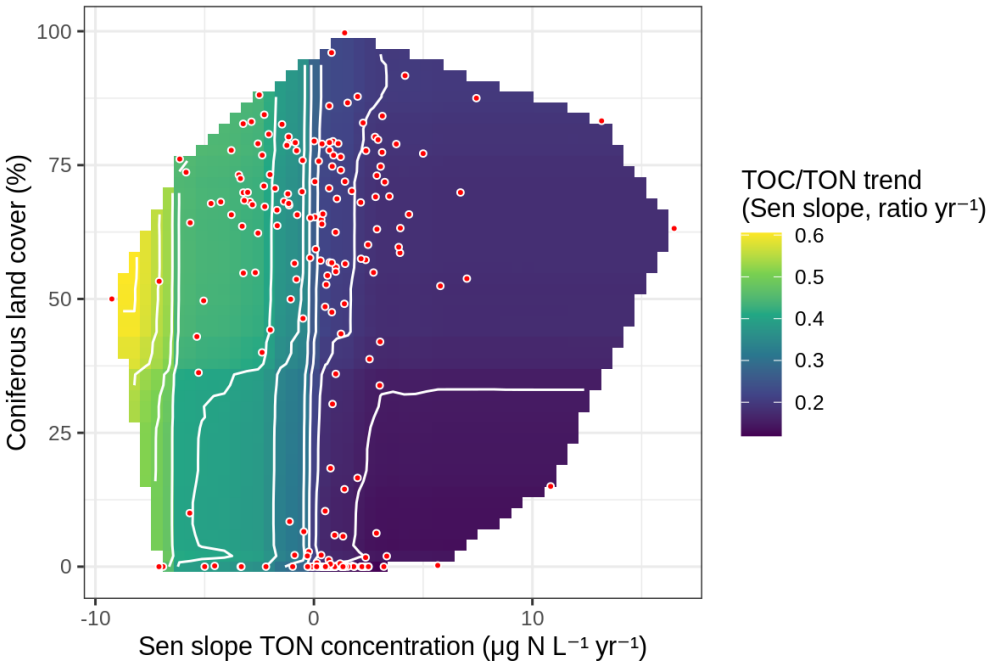

Figure 33. Predictor diagram for the variables **Sen slope TON concentration 1992-2016** and **percentage coniferous forest in catchment**. The colours indicate expected trend in TOC/TON ratio (Sen slope, 1992-2016) for a given combination of predictor variable values. The red dots represent the ICP Waters sites included in the analysis.

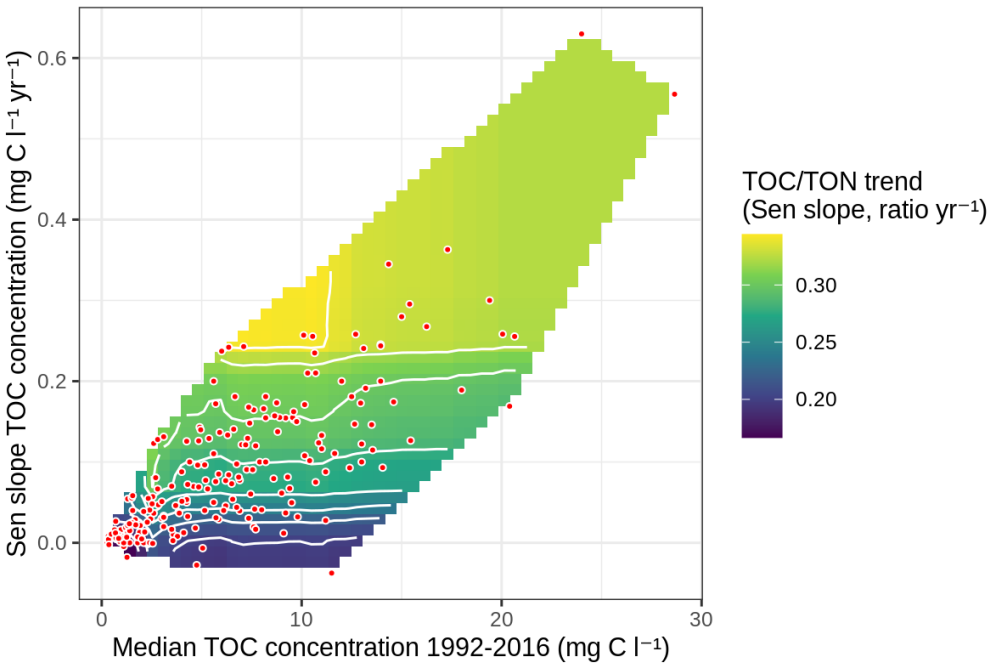

Figure 34. Predictor diagram for the variables **median TOC concentration 1992-2016** and **Sen slope TOC concentration 1992-2016**. The colours indicate expected trend in TOC/TON ratio (Sen slope, 1992-2016) for a given combination of predictor variable values. The red dots represent the ICP Waters sites included in the analysis.

4 Discussion

4.1 Possible explaining factors for trends and spatial variation in surface water NO_3 concentrations

With data from a large number of sites across Europe and North America back to the early 1990s, the ICP Waters dataset provides an excellent opportunity to study the long-term effects of N deposition on surface water chemistry. In the most recent ICP Waters trend report, Garmo et al. (2020) presented trends in NO_3 concentrations at nearly 500 ICP Waters sites in Europe and North America for the period 1990-2016.

The overall pattern presented by Garmo et al. (2020) was that NO_3 has declined in all regions. However, many of the individual sites show no trend. The greatest declines were observed in the regions with the highest NO_3 levels. Sites in East Central Europe and in the Blue Ridge Mountains (USA) had the largest decrease (58-78%) in median NO_3 levels between 1990-1994 and 2012-2016. At sites that show a decrease in NO_3 concentrations, the slope changes were generally more prevalent during the 1990s than after 2000. A few (26 out of 491) sites showed increasing NO_3 concentrations. Eleven of these were found in the south Nordic region, whereas 7 other regions had 1-3 sites with increasing trends. The reasons for this are probably site-specific. Some catchments in the Blue Ridge Mountains, Quebec and the East Central European region have been affected by insect attacks (Garmo et al. 2020, with references therein).

The statistical analyses presented here build on the findings in the report by Garmo et al. (2020) and aim to identify factors that explain the observed trends in NO_3 concentrations at ICP Waters sites in Europe and North America over the past 25 years. The underlying question is: Why do trends in surface water NO_3 concentrations vary in response to declining N deposition levels, even among catchments that receive approximately the same amount of N from atmospheric sources? For example, at German ICP Waters sites, there is a large variability in NO_3 trends, even though the N deposition level is relatively uniform. In the Italian Alps, NO_3 concentrations remain high at some sites despite strong decreases in N deposition, probably due to N saturation caused by a prolonged period of high N deposition (Rogora 2007). And in parts of Scandinavia, some sites show increasing NO_3 trends, even though median surface water concentrations are low (<100 µg N/l) and N deposition levels intermediate or low.

With the latest efforts on completing the records on catchment characteristics, N deposition and climate parameters, it has been possible to perform a rather extensive statistical analysis of possible explanatory variables for observed long-term trends and spatial variability in surface water NO_3 concentrations. Based on the selection criteria there were 453 sites from 15 countries with valid NO_3 time series from 1992 to 2016, and 214 sites from six countries with NO_3, Tot-N and TOC concentration time series during the same period.

Various combinations of explanatory variables were tested for the different random forest analyses. One challenge was that some of the catchment/land cover and climate variables were clearly inter-related and less suitable as explanatory variables in the statistical analysis. For example, interpretation of the variable *altitude* was difficult so that it was removed from the analyses, as it partly overlapped with both land cover, temperature and in some cases N deposition. Also, TOC concentration, that was used as explanatory variable in the random forest analysis, can be associated with other explanatory variables as *percentage coniferous forest* and *peatlands*.

Spatial variation in surface water NO_3 concentrations

In the analysis of spatial variability of median 2012-2016 NO_3 concentrations there was a strong positive relationship between the NO_3 concentration levels and N deposition. Contrary to expectation, none of the land cover variables stood out as important explanatory variables for the NO_3 concentration level. In a regional study including mountain lakes in North America and Europe, Burpee et al. (2021) applied the random tree statistical analyses together with generalized additive model (GAM) analysis to identify possible factors that affect the lake's sensitivity to atmospheric N deposition. On the largest geographical scale (with all sites included) they found that dissolved inorganic N (DIN = NO_3 + NH_4) concentrations were related to N deposition and smaller scale spatial variability. Analyses performed on sub regions introduced additional predictor variables of lake sensitivity; in addition to N deposition rates, catchment characteristics such as land cover, bedrock geology, lake depth, and elevation were common predictors of DIN concentrations in lakes.

Possibly, the lack of explanatory power of land cover in the ICP Waters dataset is related to different N deposition history (cf. Garmo et al. 2020) and a predominance of forested sites in the dataset (about 50% of the sites have forest cover >75%) and differences in forest characteristics – i.e. sites with mostly coniferous forests in Europe while deciduous forests dominate in North America. Also, there were some forested sites with very high nitrate concentrations, possibly because of nitrogen saturation or because the forest is very old and leaks nitrogen (internal catchment processes, possibly evidence of nitrogen saturation). The presence of forested sites with high or low historic loadings of N could be an explanation for the lack of significant land cover effect.

Trends in surface water NO_3 concentrations

The trend analyses showed that surface water NO_3 concentrations decreased at 46% of the sites, increased at 4% of the sites and showed no significant trend at the remaining 50% of the sites. The random forest analysis showed that the greatest decline in surface water NO_3 concentrations occurred at sites with high N deposition and high NO_3 concentrations in surface waters. Correspondingly, where median deposition was small, the probability of a significant decrease in NO_3 concentration was low. Many high-deposition sites have experienced significantly reduced NO_3 concentrations in surface waters during the last 10–20 years (Kopáček et al. 2005; Eshleman et al. 2013; Vuorenmaa et al. 2018; Oulehle et al. 2021a). These observations are also in line with roof experiments conducted in the European NITREX project (Tietema et al. 1998), where N deposition was excluded at a number of small forested sites with high ambient N deposition. Decreased N input at the experimental sites resulted in rapid and large reductions in NO_3 concentrations in drainage water.

The random forest analysis suggests that sites with a very high percentage of coniferous forest (>90%) have a slightly higher probability for a downward trend in NO_3 concentrations. A large majority (>80%) of these sites are located in Central Europe (mainly Germany and Czech Republic) where N deposition levels are high and show downward NO_3 trends. Therefore, the percentage of forest cover does not appear to be a direct explaining factor for declining NO_3 trends in this case, but rather a surrogate for the magnitude and long-term trend of N deposition. There are several reports on declining NO_3 trends from forested catchments in Central Europe supporting this (Vuorenmaa et al. 2018; Oulehle et al. 2021a) but also a few examples of increasing trends that can be attributed to ecosystem disturbances such as droughts or insect attacks (Eshleman et al. 1998; Oulehle et al. 2019).

The statistical analysis also indicates that declines in NO_3 concentrations are likely to happen in systems with very low TOC concentrations (<1 mg C/l). ICP Water sites with such low TOC concentrations are mainly found in the alpine mountainous areas as e.g., the Tatra Mountains in Slovakia and Poland, the Swiss and Italian Alps, and high-elevation lakes in Norway. Although there is a positive correlation between median TOC concentrations and percentage coniferous forest in the catchments (**Figure 13)**, probably linked to the soil C pool, median TOC and percentage coniferous forest pull in different directions as explanatory variables for trends in surface water NO_3 concentrations in this analysis. At a first glance this seems like a contradiction, but as explained in the previous section most of the sites with very high coverage (>90%) coniferous have a specific N deposition history. TOC concentration, on the other hand, may be seen as a proxy for soil C pools and thus 'N retention capacity'. Systems with very low TOC concentration are likely to have shallow soils and consequently a more rapid response to declines in N deposition in terms of reduced NO_3 concentrations.

In general, there is a reciprocal relationship between TOC and NO_3 concentrations in surface waters; sites with high TOC have low NO_3 whereas most sites with high NO_3 have low-intermediate TOC (e.g., Skjelkvåle et al. 1996). TOC concentration can be a proxy for *coniferous forest* and *peatlands* and may also be associated with catchment characteristics such as soil depth, which may be linked to systems with high capacities to utilise and retain N. There might also be more direct, mechanistic links between TOC and NO_3. Evans et al. (2006) pointed out that inverse patterns between NO_3 and dissolved organic carbon (DOC) may reflect spatial patterns in soil C status and N immobilization capacity, and Goodale et al. (2005) proposed that long-term decreases in stream NO_3 in eastern US could partly be due to increased microbial immobilization or denitrification fuelled by increased loading of DOC to soils and streams. Links between soil C pools and NO_3 leaching is further discussed in the next section.

4.2 N accumulation and interaction with soil C and N processes

Long-term N deposition is expected to induce a range of changes to ecosystem processes. One of these is the accumulation of N in the soil, evident from a gradual decrease in the soil C/N ratio (Aber et al. 1989; Aber et al. 1998). This accumulation of N in the soil organic matter could in theory be reflected in the C/N ratio of the organic matter leached to surface waters. However, a decreasing trend in TOC/TON was only shown at a few of ICP Waters sites (**Figure 21**). The TOC/TON was mainly increasing, or there was no significant trend. TOC/TON increases both where TON increases and where it decreases. Moreover, the trend in TOC/TON showed no relationship with N deposition. Neither did the trend in TON (**Figure 24**).

Not surprisingly, the random forest analysis indicated that the median TOC concentration is the dominant factor explaining the median TOC/TON ratios at the ICP Waters sites. Median TON concentration, lake percentage and coniferous forest also appeared as explanatory variables, but as much less important than TOC. The analysis also indicated that the probability of increasing TOC/TON trends is highest at sites with high and increasing TOC concentrations, whereas increasing TON trends points in the opposite direction. Sites with a high percentage of coniferous forest show a higher probability of increasing TOC/TON trends, which could be expected as TOC concentrations are positively correlated with % cover of coniferous forest (**Figure 25**). Also, in-lake processes in catchments with a high percentage of lakes can reduce concentrations of DOM (Dillon and Molot 1997; Köhler et al. 2013) but it is not clear whether in-lake processes also may affect/skew TOC/TON ratios by preferential retention of either TOC or TON.

Does the TOC/TON ratio in water reflect the C/N ratio in soils?

The TOC/TON ratio in runoff water does not necessarily reflect the C/N ratio in soils. The soil is highly heterogeneous, so concentrations in the surface water may integrate better across the catchment compared to scattered soil samples. On the other hand, the characteristics of the leached water will vary depending on flow paths. Soil water DOC/dissolved organic nitrogen (DON) has been shown to decrease with depth (Sleutel et al. 2009; Inamdar et al. 2012), which has been attributed to preferential sorption of more hydrophobic DOM with higher DOC/DON in upper horizons (Lajtha et al. 2005). Topographical or weather conditions giving more lateral flow could thus give higher TOC/TON. However, if these conditions stay constant over time, this would not affect the long-term trend. Yates et al. (2019) found a positive relationship between (modelled) soil C/N and in-stream DOC/DON across different land covers.

Spatial and temporal changes in soil C/N ratios

Accumulation of N deposition in the soil organic matter pool can lead to reduced C/N ratios, or simply a build-up of organic material with unchanged C/N ratio. In a study of a large number of forested sites across Europe, Gundersen et al. (1998) found a close relationship between N deposition level, NO_3 leaching and forest floor C/N ratios. Although this study provides evidence for a relationship between N deposition levels and soil C/N ratios on a large spatial scale, there are few studies that document changes in soil C/N ratios and/or TON leaching on a temporal scale. In a long-term N addition experiment to a forested catchment at Gårdsjön, Sweden, about half of the added N went to make new organic matter and half went to lower the C/N ratio of existing organic matter (Moldan et al. 2018). There are several factors that can affect C/N ratios in soil and TOC/TON ratios in runoff water and thereby mask possible effects of accumulated N from atmospheric deposition; e.g., upward TOC trends due to reduction in sulphate deposition, re-allocation of N within the soil profile, and altered processing of C and N related to changes in climate, land use or vegetation cover.

Links to long-term TOC trend

Increasing TOC/TON trends imply a change in DOM character over time, i.e. DOM with lower N content. A possible explanation for the observed TOC/TON trends at the ICP Waters sites is linked to the increase in TOC that has been observed in large parts of eastern North America and northern and central Europe over the past few decades (Monteith et al. 2007). The topic has been widely discussed, also in papers based on data from ICP Waters sites (de Wit et al. 2021). The increase has largely been related to decreasing acid deposition (de Wit et al. 2007; Hruška et al. 2009), but partly also to climatic factors, in particular increased precipitation in the northern latitudes (de Wit et al. 2016). The reduced acid deposition gives increased pH and lower ionic strength, both of which can increase the solubility of more hydrophobic DOM (de Wit et al. 2007). Hydrophobic DOM has been shown to be more N-depleted (Lahjta et al. 2005). The effect of reduced acid deposition on DOM solubility may thus mask any potential effect of N accumulation in the soil.

Rodriguez-Cardona et al. (2022) studied DOC, DON and DOC/DON trends in streams across different biomes. They observed mostly increasing DOC and DON trends in sites historically affected by acid deposition but there was little effect on DOC/DON. Deininger et al. (2020) reported increasing TOC and TON concentrations but decreasing TOC/TON in rivers draining areas affected by acid deposition in Norway. A coupling to N enrichment of the soil organic matter was indicated, but these rivers are also affected by local anthropogenic inputs. A large-scale lake survey in the same region (southern/eastern Norway) showed significantly higher TOC/TON in 2019 compared to 1995 (de Wit et al., in prep.), which was also the case for the set of lakes from this region included in the ICP Waters dataset. In the lake survey both TOC and TON were increasing, but TOC to a larger extent.

N accumulation in different soil layers

It is difficult to document a lowering of the soil C/N ratio as a result of chronic exposure to elevated N deposition. Has the soil C/N not declined, after all? Or is the DOM not representative for the parts of the soil where most of the N accumulates? Or is a large fraction of the deposited N lost by denitrification? Elevated N deposition stimulated soil denitrification in a study of 12 mountainous catchments in the Czech Republic (Oulehle et al. 2021b). It might prevent significant lowering of soil C/N ratios calculated from soil carbon content and cumulative N loads.

When the issue of N accumulation and saturation was raised, it was hypothesized that N would accumulate in the forest floor, as a result of increased plant uptake and thus higher litter N content (Aber et al. 1989). There are few long-term records of soil C/N ratios. However, a long-term record of forest floor C/N in a northern hardwood forest at Hubbard Brook, New Hampshire, showed a slight increase, but neither the results from this or nearby forests indicated an accumulation of N in the forest floor (Yanai et al. 2013). They argue that the excess N is rather accumulating in the mineral soil or lost as gaseous compounds via nitrification or denitrification.

Various ^{15}N tracer studies have showed that the soil organic horizon is an important sink during the first 7-8 years (Nadelhoffer et al. 2004; Wessel et al. 2013) or up to 14 years after application (Krause et al. 2012). For the Wessel et al. (2013) study, another 11 years of monitoring showed a decrease in the ^{15}N recovery in the organic soil and an increase in the mineral soil (Wessel et al. 2021). In a study of four sites, two decades after ^{15}N addition (Veerman et al. 2020) two sites showed higher recovery in the mineral than the organic soil. This suggests a gradual transport of N from the organic to the mineral soil, but the distribution appears to depend on soil and site characteristics as well as the N deposition level. Over time one might thus expect that a decline in soil C/N is most evident in the mineral soil, while the organic soil to a larger extent may reflect more recent deposition levels.

If the trend in soil C/N is different in the organic and mineral soil, the source of the DOM becomes important when interpreting TOC/TON trends in runoff. If the TOC/TON mainly originates from organic layer DOM, one may not expect it to decrease over time. DOM levels are generally higher in the organic top layer, and despite DOM sorption in the mineral soil, the DOM in the surface waters may thus still be dominated by DOM from the organic top layer. Moreover, increased precipitation and high-intensive rainfall due to climate change may give more lateral flow, preventing sorption of DOM in deeper soils and further increase leaching of DOM from the upper part of the soil profile. Hence, the increasing trend or lack of trend in TOC/TON at the ICP Waters sites could potentially be explained by limited long-term accumulation of N in the organic soil and a high and possibly increasing fraction of the DOM originating from this part of the soil profile.

4.3 What might happen with accumulated N in the long term?

The concept of “N saturation” in terrestrial ecosystems was introduced in 1989 by Aber et al. (1989) and is indicated by increased leaching of NO_3 or NH_4 below the rooting zone. Such increases in inorganic N are manifest by elevated concentrations in surface waters. Aber et al. (1989) pointed out that chronic elevated deposition of inorganic N could cause N saturation.

Increased leaching of NO_3 from soil to water can have an acidifying effect on runoff water (Reuss and Johnson (1986), eutrophying effects in marine waters, and possibly also in certain freshwater bodies (Elser et al. 2009; Lepori & Keck 2012). Whereas terrestrial ecosystems generally are regarded as N-limited and freshwater ecosystems as P-limited, there are an increasing number of studies indicating

that N can be a limiting nutrient in oligotrophic surface waters (Elser et al. 2009; Thrane et al. 2021, with references therein). In an analysis based on a Nordic lake dataset and a Norwegian river dataset on water chemistry from Norwegian rivers, Thrane et al. (2021) found that N limitation of algal growth seems to prevail in surface waters that receive low N deposition and that elevated N deposition can shift an ecosystem from N to P limitation.

In the 1990s, synoptic data from forest ecosystems in Europe pointed to two "thresholds" for N saturation. At N deposition greater than about 9 kg N ha^{-1} yr^{-1} (lower threshold) some sites had significant concentrations of NO_3 in runoff. At N deposition greater than 25 kg ha^{-1} yr^{-1} (higher threshold) all sites had significant concentrations of NO_3 in runoff (Dise and Wright 1995). Gundersen et al. (1998) linked NO_3 concentration in leachate to the C/N ratio in the organic horizons of forest soil. The implication of the synoptic data from forest ecosystems in Europe was thus that chronic N deposition over time would lead to accumulation of N in soil and lower C/N ratios. The forest would move from N-poor to N-rich and begin to lose N as NO_3 to leachate and surface water (Dise et al. 1998). A study on long-term trends (1999-2010) in bulk precipitation and throughfall at several hundred ICP Forest plots showed only slight decreasing trends for inorganic N and stated that further reduction of N emissions would be needed to avoid acidification and eutrophication in European forests (Waldner et al. 2014).

Based on the present analysis, the ICP Waters data are consistent with the synoptic picture from the 1990s. The NO_3 concentration data for the period 2012-2016 again point to an N deposition "threshold" of about 10 kg N ha^{-1} yr^{-1} (1000 mg m^{-2} yr^{-1}) below which very little NO_3 is leached (Figure 4). However, NO_3 data from the ICP Waters sites do not show signs of large-scale N saturation over the 25-year period 1992-2016. The majority of the sites show either decreasing concentrations of NO_3 or no significant trend. This is in line with results from other regional studies in North America and Europe (Eshleman et al. 2013; Garmo et al. 2014; Vuorenmaa et al. 2018; Hindar et al. 2020). Further, the data do not suggest that many sites have moved from N-limited to N-saturated over the 25-year period, despite having N deposition rates during this period well above the 9 kg N ha^{-1} yr^{-1} threshold. And this holds both for sites in forested catchments and for sites in non-forested catchments.

Only 19 of the 453 sites with valid NO_3 time series had statistically significant increases in NO_3 concentrations over the 25-year period 1990-2016. Of these, two sites (in Bohemian Forest, CZ and Bayrische Wald, DE) had high median NO_3 concentrations (> 600 µg N l^{-1}). Here, the increasing NO_3 trends are caused by bark beetle (*Ips typhographus*) massive infestation in the 2000´s and subsequent Norway spruce forest dieback. Decomposition of large amounts of fresh dead biomass resulted in large NO_3 (as well as base cations and Al) leaching from soil to surface waters (Oulehle et al. 2019). Thus, the observed upward trends were not a result of enhanced N deposition in this case. The 17 remaining sites had low median NO_3 concentrations (< 100 µg N l^{-1}), which means that relatively small changes in concentrations can lead to significant time trends. Given the low median NO_3 concentrations, it is unlikely that the increasing trends are explained by the ambient N deposition levels but rather a result of other confounding factors such as forest age, harvesting, or climate change.

The current situation is that N deposition is generally declining over large parts of Europe and North America, as a result of long-term and international efforts to reduce emissions of acidifying compounds and greenhouse gases. So far, however, the emission reductions have been largely in oxidised N, whereas emissions of reduced N (ammonia, NH_3) have lagged somewhat behind (European Environment Agency, 2021). Reduced N comes mainly from agriculture. Different

progression in emission reductions of oxidised and reduced N has resulted in higher relative importance of reduced N (as NH_4) in deposition (Li et al. 2016; Rogora et al. 2016). This may have implications for catchment N retention (and enrichment), as NH_4 is more easily retained than NO_3.

Losses of total N (sum of NO_3, NH_4, TON) from soils to surface waters are usually much less than the total inputs via atmospheric N deposition. In a mass-balance study based on 30 years with input-output data from four small catchments in southern Norway, TN outputs to the stream constituted 30-50% of the total atmospheric inputs (Kaste et al. 2020). Loss via denitrification was an unknown factor in these budgets but assumed to be low as the catchments mainly consisted of well-drained soils. This implies that the catchments continue to accumulate N in soil and vegetation, even though atmospheric N inputs show declining trends. This is probably the case also in many of the ICP Waters sites.

The N deposition retained in the catchment may (1) be built into new aboveground or belowground biomass, both by increasing the volume of biomass and by enriching biomass with N, (2) be stored in the soil either as new organic matter with unchanged C/N ratio or by lowering the C/N ratio of the existing soil, and (3) be released to the atmosphere via denitrification (Curtis et al. 2012; Oulehle et al. 2021b). At a long-term experimental N addition to a whole forested catchment at Gårdsjön, Sweden, after 12 years of N addition about 40% went to biomass, 10% went to runoff, and the remaining 50% most probably to soil. Of the N accumulated in the soil, a rough estimate is that about half of the added N went to make new organic matter and half went to lower the C:N ratio of existing organic matter (Moldan et al. 2018).

Lowering of the C:N ratio in soil organic matter may in the long-term lead to ‘‘N saturation’’, with elevated leaching of NO_3 to stream water. As data from a large share of ICP Waters sites show decreasing NO_3 trends in surface waters and an increase in C/N ratio of DOM, there are few indications that N saturation is occurring here and now. However, there are sites with old-growth or disturbed forests in high-deposition areas that can be at risk. Also, climate change can pull in both directions; increased terrestrial productivity due to increased temperature and longer growing season will imply a higher demand for N from plants and lower likelihood for N saturation, whereas more intensive rainfall, severe droughts and higher risk for insect attacks can promote higher N leaching from terrestrial ecosystems.

4.4 Uncertainties

Although the ICP Waters dataset contains long-term data from a large number of sites covering a wide geographical area, it also has inherent inconsistencies that sometimes makes it difficult to draw firm conclusions regarding temporal and spatial variation in N dynamics and possible regulating factors. All N species are not analysed at all sites, and the sampling frequency and length of the time series vary from site-to-site and from country-to-country. It is a mixture of lake and stream sites with catchments ranging from < 1 to nearly 2000 km^2. The geographical distribution and site density vary highly among the countries. The dataset is dominated by sites in Canada, the US, Norway and Sweden. There are also several sites from Finland and the United Kingdom, but fewer from other parts of Europe.

When selecting sites for the statistical analysis, there was a trade-off between completeness of the data from the individual sites and geographical representativity. Firstly, sites were selected based on the availability of water chemistry data. Many sites lack analyses of NH_4, particularly in the long time series, so TON was calculated as Tot-N minus NO_3. Also, many countries do not analyse Tot-N and

TOC. Hence, there were far fewer sites with available TOC/TON data compared to the number of sites with complete NO_3 data.

Some of the catchment characteristics were not reported for every site, and this reduced the number of sites that could be included in the random forest analysis of NO_3 trends from 453 to 423 sites. A larger challenge for the statistical analysis was that some of the potential explanatory variables were intercorrelated or varied systematically between regions/continents, in such a way that they were less suitable as explanatory variables in the statistical analysis. For example, forests are dominated by deciduous trees in North America and coniferous trees in Europe, while the N deposition history is also systematically different between the continents (reductions occurred later in North America compared with Europe (Garmo et al. 2020)).

A possible way to overcome this would be to perform individual statistical analyses on different spatial scales (hemispheric, regional, sub-regional) as done by Burpee et al. (2021) in an analysis of North American and European mountain lake ecosystems and their sensitivity to atmospheric N deposition. However, this would imply an extension of the work that would be beyond the scope of the current analysis.

Despite these shortcomings, the ICP Waters dataset provides an excellent opportunity to study the long-term effects of N deposition on surface water chemistry – over time and on a large geographical scale. It is therefore important to continue actively collecting new data, harmonizing parameters, and supplementing the ICP Waters database with new land cover data and information on catchment characteristics.

5 Conclusions

The report presents statistical analyses of controls (deposition, land cover, climate) of spatial variability and long-term trends in surface water concentrations of NO_3 and C/N ratios of DOM at the ICP Waters sites. A trend analysis is combined with a statistical classification method called "random forest analysis", where we seek to explain the response variable using a set of predictor variables. The trend analyses include 453 sites from 15 countries with valid NO_3 time series from 1992 to 2016, and 214 sites from six countries with NO_3, Tot-N and TOC concentration time series during the same period.

The analysis of spatial variability of median 2012-2016 NO_3 concentrations in surface waters showed a strong positive relationship with N deposition level. On a regional scale, none of the land cover variables stood out as important explanatory variables for the NO_3 concentration level. This is surprising and could be related to a predominance of forested sites in the dataset (about 50% of the sites have forest cover >75%) and differences in forest characteristics and N deposition history between regions.

Over the period 1992-2016, surface water NO_3 concentrations have decreased significantly at 46% of sites, while 50% of the sites showed no significant trend. A few sites (4%) show increasing NO_3 concentrations, at most sites probably due to site-specific factors or disturbances and not by the ambient N deposition levels itself. The statistical analysis showed that median NO_3 concentrations, median N deposition, and to a lesser degree percentage of coniferous forest and median TOC concentration, were important factors in explaining observed time trends in NO_3 concentrations.

The analysis of spatial variability of median 2012-2016 TOC/TON ratios at the ICP Waters sites indicated that the median TOC concentration was the dominant explanatory factor. Median TON concentration, lake percentage and coniferous forest also appeared as explanatory variables, but as much less important than TOC.

Trends in TOC/TON ratios in surface water during 1992-2016 were mainly increasing, or there was no significant trend. The trend in surface water TOC/TON ratios showed no relationship with N deposition. Neither did the trend in surface water TON. The random forest analysis indicates that the probability of increasing TOC/TON trends is highest at sites with high and increasing TOC concentrations, whereas increasing TON trends points in the opposite direction. Sites with a high percentage of coniferous forest show a higher probability of increasing TOC/TON trends, which could also be expected as coniferous forest is positively correlated with median TOC concentrations.

Results from the present analysis of ICP Waters data are consistent with previous studies that have pointed at a N deposition "threshold" of about 10 kg N ha^{-1} yr^{-1}, below which very little NO_3 is leached. The current situation seems to be that N deposition is generally declining over large parts of Europe and North America, and that that NO_3 concentrations in surface water have declined in all regions, although many of the individual sites show no trend.

The present data from ICP Waters do not suggest that N saturation is occurring here and now, but there are sites with old-growth or disturbed forests in high-deposition areas that can be at risk. Climate change can pull in both directions by increasing the primary productivity and demand for N but might also promote increased N leaching linked to intensive rainfall, severe droughts and higher risk for insect attacks. Although the N deposition has been reduced in recent years, ambient loads

might still exceed long-term sustainable levels and perhaps cause N saturation further into the future.

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