



Global Biogeochemical Cycles

RESEARCH ARTICLE

10.1002/2017GB005749

Key Points:

- Fe has increased significantly in 28% of the 340 studied waters by on average 64% between 1990 and 2013
- Most increasing trends and the highest rate of change were found in the boreal region of northern Europe
- Hydrological changes may have contributed to the observed Fe trends. Trends may also be linked to declining atmospheric S deposition

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Citation:

Björnerås, C., Weyhenmeyer, G. A., Evans, C. D., Gessner, M. O., Grossart, H.-P., Kangur, K., ... Kritzberg, E. S. (2017). Widespread increases in iron concentration in European and North American freshwaters. *Global Biogeochemical Cycles*, 31, 1488–1500. <https://doi.org/10.1002/2017GB005749>

Received 22 JUN 2017

Accepted 9 SEP 2017

Accepted article online 5 OCT 2017

Published online 20 OCT 2017

Widespread Increases in Iron Concentration in European and North American Freshwaters

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Abstract Recent reports of increasing iron (Fe) concentrations in freshwaters are of concern, given the fundamental role of Fe in biogeochemical processes. Still, little is known about the frequency and geographical distribution of Fe trends or about the underlying drivers. We analyzed temporal trends of Fe concentrations across 340 water bodies distributed over 10 countries in northern Europe and North America in order to gain a clearer understanding of where, to what extent, and why Fe concentrations are on the rise. We found that Fe concentrations have significantly increased in 28% of sites, and decreased in 4%, with most positive trends located in northern Europe. Regions with rising Fe concentrations tend to coincide with those with organic carbon (OC) increases. Fe and OC increases may not be directly mechanistically linked, but may nevertheless be responding to common regional-scale drivers such as declining sulfur deposition or hydrological changes. A role of hydrological factors was supported by covarying trends in Fe and dissolved silica, as these elements tend to stem from similar soil depths. A positive relationship between Fe increases and conifer cover suggests that changing land use and expanded forestry could have contributed to enhanced Fe export, although increases were also observed in nonforested areas. We conclude that the phenomenon of increasing Fe concentrations is widespread, especially in northern Europe, with potentially significant implications for wider ecosystem biogeochemistry, and for the current browning of freshwaters.

1. Introduction

A handful of recent studies report on strong increases in iron (Fe) concentrations in freshwaters in northern Europe (Knorr, 2013; Kritzberg & Ekstrom, 2012; Neal et al., 2008; Sarkkola et al., 2013; Weyhenmeyer, Prairie, & Tranvik, 2014). Fe is the fourth most abundant element of the Earth's crust and an essential micronutrient that is tightly connected to the biogeochemical cycling of carbon, nitrogen, and phosphorus in aquatic ecosystems (Stumm & Morgan, 1996). This includes the suggested function of Fe as a “rusty sink” of organic carbon in both freshwater and marine sediments (Lalonde et al., 2012). There is also evidence that Fe contributes to the ongoing large-scale browning of freshwaters (Kritzberg & Ekstrom, 2012; Weyhenmeyer et al., 2014), which until recently has been attributed mainly to increasing concentrations of dissolved organic carbon (Erlandsson et al., 2008; Haaland et al., 2010; Hongve, Riise, & Kristiansen, 2004; Monteith et al., 2007). Furthermore, Fe is recognized as an important component of the biological carbon pump in the ocean,

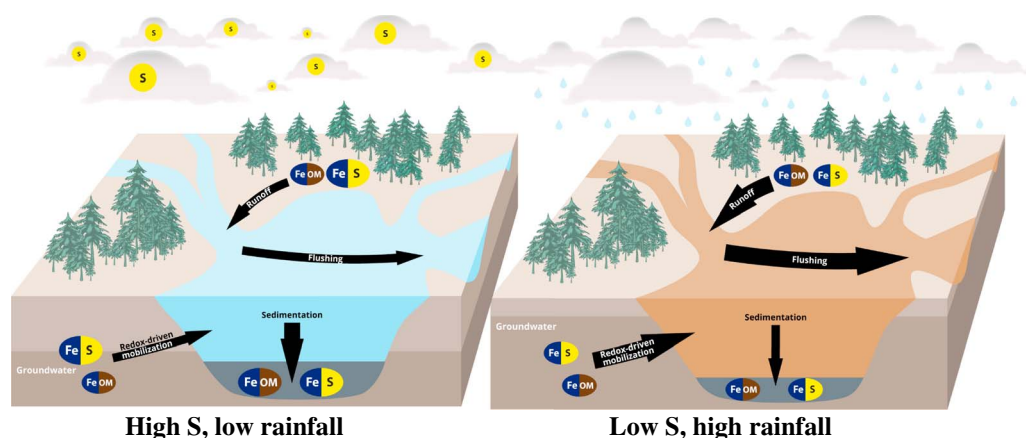


Figure 1. Effects of sulfur (S) deposition and precipitation on Fe mobility. (left) Under a high S deposition scenario, Fe binding to sulfides in soils could reduce Fe export from catchments to surface waters. Similarly, Fe sulfides may accumulate in sediments, resulting in less Fe in the water column of the lake and clearer water. (right) In the wet-climate scenario with less reactive S, more intense precipitation increases runoff from the catchment, flushing rates through lakes, and redox-driven mobilization of Fe in the soils as a result of a raised groundwater table. The resulting increases in Fe associated with organic matter lead to surface water browning.

where Fe commonly limits phytoplankton growth in waters rich in nitrogen and phosphorus (Boyd et al., 2007; Martin & Fitzwater, 1988; Moore et al., 2013). While salinity-induced flocculation and sedimentation is generally thought to efficiently trap Fe in coastal areas, recent work suggests that river-derived humic substances may stabilize Fe and act as a carrier that transports Fe far offshore (Krachler et al., 2015; Kritzberg, Villanueva, et al., 2014; Laglera & van den Berg, 2009; Pokrovsky & Schott, 2002). These multifaceted roles of Fe suggest that changes in concentrations are likely to have significant and diverse effects on regional and global biogeochemical cycles. Thus, it is important to develop a better understanding of the frequency and spatial distribution of temporal trends in Fe concentrations in surface waters, as well as of the factors and mechanisms governing Fe dynamics.

Few previous freshwater studies consider temporal changes in Fe concentration, and these tend to be spatially restricted. In Swedish river mouths, for example, Fe concentrations have on average doubled during the past four decades (Kritzberg & Ekstrom, 2012), and high rates of change in Fe concentration have also been reported for streams and lakes in the UK (Neal et al., 2008), headwaters in Finland (Sarkkola et al., 2013), and a single river catchment in Germany (Knorr, 2013). These increases in Fe concentration in freshwaters may be the result of two processes: (i) increasing export of Fe from the catchment and (ii) changes in biogeochemical cycling of Fe within the aquatic environment (Figure 1). Both processes could be substantially affected by increases in precipitation as projected by several climate change scenarios. Increasing surface and subsurface water runoff following more frequent and more intense precipitation events can enhance Fe transport from soils to aquatic ecosystems (Hongve et al., 2004). Since Fe is a redox-sensitive element with enhanced solubility during reducing conditions, more frequent waterlogging of soils may enhance microbial activity that promotes reducing conditions and the release of Fe (Knorr, Lischeid, & Blodau, 2009), particularly when alternative electron acceptors (such as nitrate and sulfate) are lacking (Palviainen et al., 2015). A positive relationship between reducing intensity in the catchment soil and Fe concentration in receiving surface waters has been confirmed in both field studies (Ekstrom et al., 2016) and laboratory incubation experiments (Frohne et al., 2011; Grybos et al., 2007). As for the second process, faster flushing rates through standing waters driven by intense precipitation may restrain Fe sedimentation and thus result in elevated Fe concentrations in the water column (Weyhenmeyer et al., 2014). Thus, the efficiency of standing waters as Fe sinks (Einola et al., 2011; Jonsson, 1997) may decrease at present as a response to a shorter water retention in the landscape.

Declining atmospheric sulfur (S) deposition, which has occurred across northern Europe and parts of North America since the 1970–1980s (Schopp et al., 2003), may also be a potential explanation for increasing Fe concentrations in freshwaters (Figure 1). Fe^{3+} - and SO_4^{2-} -reducing bacteria can effectively compete for organic substrates (Chapelle & Lovley, 1992), such that reduced input of SO_4^{2-} may favor Fe reduction,

while Fe also forms stable precipitates with sulfide which may reduce Fe leaching under S-rich conditions (Morse et al., 1987). These processes could have enhanced binding of Fe in soils and sediments during the peak of S deposition, resulting in a higher release of Fe into groundwater and surface waters during the last decades when the availability of S has declined. Declining acid deposition may also have an indirect effect on Fe concentrations by mobilizing more dissolved organic matter (DOM) to surface waters, which could enhance the solubility and transport rates of Fe to surface waters (Neal et al., 2008).

Notwithstanding that Fe is a key element in global biogeochemical processes our present knowledge of the extent and rate of Fe changes in freshwaters, or the associated driving mechanisms, remains sparse. Here we analyzed temporal trends in Fe concentrations across lakes, headwater streams, higher-order streams, and river mouths in northern Europe and North America to gain a better understanding of factors influencing rising Fe concentrations. Using changes in silica (Si) concentrations in freshwaters as a proxy for changes in hydrological pathways, and decreasing sulfate (SO_4) concentrations in freshwaters as a proxy for declining atmospheric S deposition, we hypothesized that increasing Fe concentrations in freshwaters would covary with increasing Si concentrations and decreasing SO_4 concentrations.

2. Methods

We analyzed monitoring data from a total of 340 freshwater bodies, of which 90 were located in Sweden, 24 in Norway, 59 in Finland, 7 in Estonia, 2 in Latvia, 5 in Germany, 5 in the Czech Republic, 21 in the UK, 77 in Canada, and 50 in the U.S. The waters include headwater streams (35), higher-order streams (including rivers) (85), lakes (168), and river mouths (63). Since the time series in the original data sets varied in length, we restricted our analyses to the time period between 1990 and 2013 to make the final global data set as homogeneous as possible. In addition to the global data set we analyzed the Swedish data set separately to confirm observed patterns, since this represented the largest single data set, with internally consistent methods and time period.

The analytical methods used to determine Fe at different locations include (1) inductively coupled plasma (used for Sweden, Finland, Norway, the UK, the U.S., and Canada (Nova Scotia)), (2) inductively coupled argon plasma (Canada (Nova Scotia)), (3) atomic absorption spectroscopy (Sweden, Finland, Latvia, the Czech Republic, the U.S., and Canada (Ontario and Nova Scotia)), and (4) flow injection analysis (Finland and Germany). Notably, for some systems there has been a change in the analytical method applied over time, but since we apply here nonparametric methods (see below) we consider that the effects of the analytical method changes on our main results should be minor. Moreover, for some systems the detection limit was lower in the latter part of the time series. To avoid biases in the trend analyses resulting from the detection of lower concentrations in recently collected data, the detection limit was adjusted to be consistent over the entire period at any given location.

In addition to Fe concentrations, we also compiled surface water data on three chemical variables (total/dissolved organic carbon (OC), sulfate (SO_4), and Si (reactive silica, SiOx)). We used temporal variations in SO_4 concentrations as a proxy for changes in atmospheric S deposition (Monteith et al., 2007) and temporal variations in Si concentrations as a proxy for changes in hydrological pathways, where wetter conditions enhance flow through intermediate soil depths rich in Si and Fe (Smedberg et al., 2006). This approach is suitable for mineral soils but not for peatlands and wetlands. Since the catchments of most of our waters (>85%) mainly consist of mineral soils, we consider our approach suitable but we are aware that deviations of common global patterns might be a result of deviating soil properties.

We also obtained annual precipitation and air temperature data from 1990 to 2013 from the following institutions: the Swedish Meteorological and Hydrological Institute; Norwegian Meteorological Institute (MET Norway); Finnish Meteorological Institute; Weather Service at the Estonian Environment Agency; Latvian Environment, Geology, and Meteorology Center; Deutscher Wetterdienst and Federal Environmental Agency (Germany); the UK Environmental Change Network; the Czech Hydrometeorological Institute; Environment and Climate Change Canada (Ontario and Nova Scotia); and the National Centers for Environmental Information of the National Oceanic and Atmospheric Agency (U.S.). Additionally, we obtained data on 10 climate and catchment variables (latitude, longitude, altitude, water body type, catchment size, site-specific annual mean air temperature (average 1961–1990), site-specific annual precipitation (average 1961–1990), percent of lake surface cover in the catchment area, percent of agricultural land in catchment,

Table 1
Freshwaters Showing Significant Changes in Yearly Median Fe Concentration Between 1990 and 2013^a

Region	System	No. of sites	% + Fe	% – Fe
Fennoscandia	Headwater	15	13.3	0.0
Fennoscandia	Higher-order stream	30	60.0	0.0
Fennoscandia	Lake	65	41.5	6.2
Fennoscandia	River mouth	63	34.9	1.6
	All systems	173	39.9	2.9
Europe ^b	Headwater	30	20.0	3.3
Europe ^b	Higher-order stream	33	57.6	0.0
Europe ^b	Lake	87	42.5	5.7
Europe ^b	River mouth	63	34.9	1.6
	All systems	213	39.4	3.3
North America	Headwater	5	0.0	20.0
North America	Higher-order stream	41	7.3	7.3
North America	Lake	81	9.9	4.9
North America	River mouth			
	All systems	127	8.7	6.3
All sites	Headwater	35	17.1	5.7
All sites	Higher-order stream	74	29.7	4.1
All sites	Lake	168	26.8	5.4
All sites	River mouth	63	34.9	1.6
	All systems	340	27.9	4.4

^aSignificant positive and negative trends in Fe concentration over time were identified using Mann-Kendall trend tests and the Theil-Sen slope estimator. ^bEurope includes Fennoscandian sites.

and percent of upland coniferous forest in the catchment). Since not all variables were available for every location, a number of data points vary slightly among different analyses.

The significance of Fe temporal trends was tested by applying the non-parametric Mann-Kendall trend test to yearly median values during 1990 to 2013. Absolute rates of change ($\text{mg L}^{-1} \text{yr}^{-1}$) were determined by using the Theil slope of the Mann-Kendall trend test (Dery et al., 2009; Stahl et al., 2010; Theil, 1950). Relative rates of change ($\% \text{yr}^{-1}$), hereafter abbreviated as ΔFe , were calculated by dividing the Theil slope with the long-term (1990–2013) median concentration and multiplying the result by 100.

Partial least squares (PLS) regression models were used to predict the variance of ΔFe as a result of variation in water chemistry (absolute and relative changes as well as long-term median concentrations), climate and catchment variables as explanatory variables. PLS ranks explanatory variables according to their relevance in explaining variation in the response variable (Wold, Sjostrom, & Eriksson, 2001). The ranks are expressed as variable importance in projection (VIP) values, where the most important variable for the model performance is assigned the highest VIP value. Explanatory variables with a VIP value >1.0 are considered important for the model performance (Wold et al., 2001). The PLS analyses were carried out in the JMP package, version 12.0.

Significant relationships between water chemistry and catchment variables were explored by nonparametric correlation analyses (Kendall's

tau). Furthermore, we used the nonparametric Wilcoxon test for group comparisons between headwater streams, higher-order streams, lakes, and river mouths. Correlations and group-comparison tests were performed using IBM SPSS Statistics 23.

3. Results

3.1. Iron and Other Solute Concentration Changes

We found significant increases in Fe concentration from 1990 to 2013 in 28% of the 340 North European and North American water bodies (Table 1). Most of the sites showing significant positive Fe trends were located in Europe with only a few in North America (Table 1 and Figure 2).

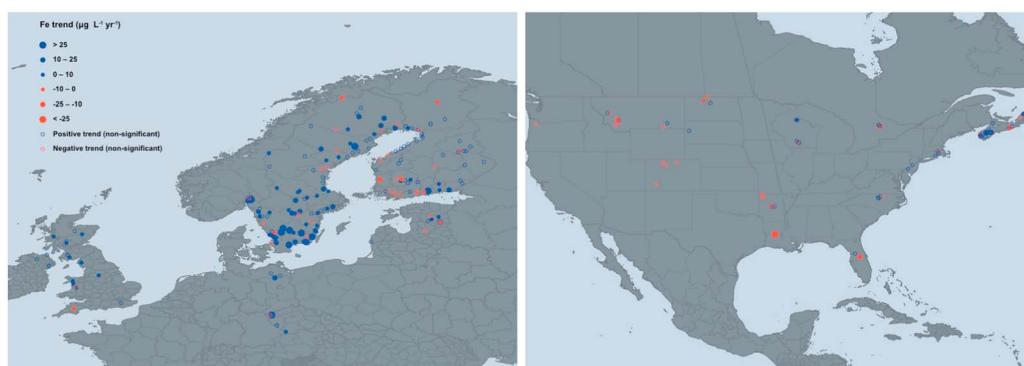


Figure 2. Changes in Fe concentration in (left) European and (right) North American freshwaters between 1990 and 2013. Blue circles represent positive and red circles represent negative trends in Fe concentrations. The size of the circles reflects the magnitude of the changes. Filled circles denote significant trends, and open circles denote nonsignificant changes. Some symbols are overlapping due to water bodies located closely to each other.

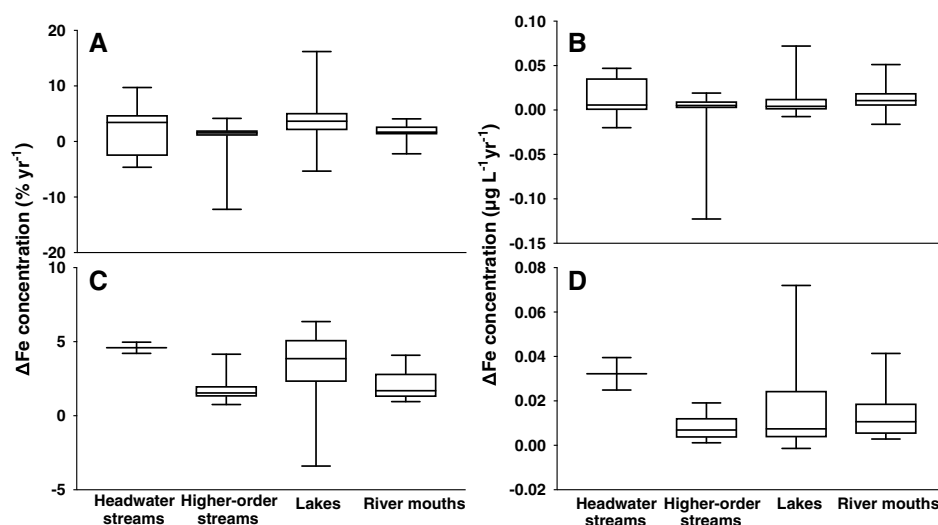


Figure 3. Median Fe changes in four different types of water bodies. (a) Relative and (b) absolute Fe changes for all waters. (c) Relative and (d) absolute Fe changes for Swedish waters. The boxes represent the 25th and 75th percentiles, and the whiskers represent the minimum and maximum values. Only systems where Fe has changed significantly during the study period (1990–2013) were included in the analyses.

The absolute rate of change in Fe concentrations during 1990 to 2013 ranged from -123 to $+72 \mu\text{g L}^{-1} \text{yr}^{-1}$ (median $1 \mu\text{g L}^{-1} \text{yr}^{-1}$) for all 340 sites. This absolute rate of change corresponded to a ΔFe range from -13.7 to $+16.2\% \text{yr}^{-1}$ (median $0.8\% \text{yr}^{-1}$). For the sites with significant positive ΔFe , the median change in Fe concentration for the entire 23 year period was 61% (standard deviation 55%) and the maximum measured increase was 373%. Since the absolute rate of change is positively correlated to long-term median concentrations (Kendall’s tau, $T_b = 0.23, p < 0.001$), the spatial variation in Fe trends (Figure 2) also gives an indication of regional differences in average Fe concentration.

Analyzing standing and running waters separately we found a similar frequency of positive trends between the water types (Table 1). However, mean ΔFe was significantly higher for lakes than for higher-order streams

Table 2
Partial Least Squares Regression (PLS) Model Predicting ΔFe ($\% \text{yr}^{-1}$) by a Variety of Water Chemistry and Catchment Variables (X)

X	VIP	VIP ^a
Si, absolute change	2.20	1.54
Si, relative change	2.13	1.38
Percent of conifers in catchment	1.66	1.64
Site-specific long-term (1961–1990) annual mean air temperature	1.40	1.60
SO ₄ , relative change	1.37	1.19
SO ₄ , long-term median	0.84	0.79
OC, relative change	0.73	0.74
Si, long-term median	0.60	0.91
Longitude	0.53	0.59
Size of catchment area (km ²)	0.51	0.72
Percent of open water in the catchment	0.49	0.50
OC, long-term median	0.46	0.74
Percent of agricultural land in catchment	0.45	0.48
SO ₄ , absolute change	0.33	1.09
Altitude (m)	0.25	0.73
OC, absolute change	0.20	0.81
Site-specific long-term (1961–1990) annual precipitation (mm)	0.14	0.64
Latitude	0.13	0.76
Fe, long-term median	0.07	0.92

Note. VIP values above 1 show important x variables. ^aOnly sites with significant ΔFe were included in the analysis.

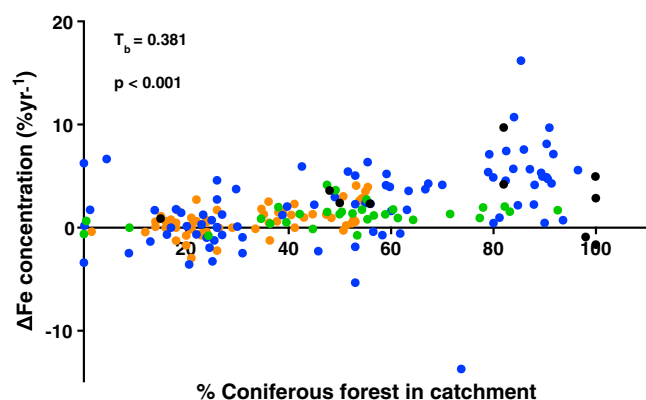


Figure 4. Relationship between ΔFe and the percentage of coniferous forest in the catchment ($N = 184$). T_b is the correlation coefficient Kendall's tau- b . Symbols represent data for headwater streams (black), higher-order streams (green), lakes (blue), and river mouths (orange).

and river mouths (Wilcoxon test: $p < 0.01$; Figure 3a). Since all river mouths in this study are located exclusively in Sweden and Finland the observed differences between water types are potentially confounded by a geographical bias. However, when restricting the comparison to Swedish sites, ΔFe was still significantly higher in lakes than in higher-order streams and river mouths (Wilcoxon test: $p < 0.01$ for both comparisons; Figure 3c). In addition, for Swedish waters, headwater streams showed significantly higher ΔFe compared to both higher-order streams and river mouths (Wilcoxon, $p < 0.05$; Figure 3c).

As for Fe, OC concentrations also increased during 1990 to 2013. We found that OC concentrations had increased significantly in 59% of the 315 sites with OC time series. The absolute change in OC concentration ranged from $-1.6 \text{ mg L}^{-1} \text{ yr}^{-1}$ to $+5.7 \text{ mg L}^{-1} \text{ yr}^{-1}$, with a median absolute change of $0.1 \text{ mg L}^{-1} \text{ yr}^{-1}$. The relative change in OC ranged from -43.2 to $+116.7\% \text{ yr}^{-1}$, with a median change of $1.5\% \text{ yr}^{-1}$. For the sites where OC has increased significantly over time, the median increase in OC was 43% (standard deviation 23%). Hence, the median relative increase in Fe concentration was 1.4 times higher than for OC. Of the 95 sites that showed positive Fe trends, 77% also had a significant positive OC trend.

We observed a general decline in SO_4 concentrations (significant reductions in 78% and 74% of European and North American waters, respectively). Changes in SO_4 concentration for the study period were similar in the waters in Canada (median = $-0.05 \text{ mg L}^{-1} \text{ yr}^{-1}$), the U.S. ($-0.03 \text{ mg L}^{-1} \text{ yr}^{-1}$), Fennoscandia ($-0.10 \text{ mg L}^{-1} \text{ yr}^{-1}$), and the UK ($-0.07 \text{ mg L}^{-1} \text{ yr}^{-1}$), while the decline was larger in the waters in the Czech Republic ($-0.31 \text{ mg L}^{-1} \text{ yr}^{-1}$) and Estonia ($-0.33 \text{ mg L}^{-1} \text{ yr}^{-1}$). We also observed widespread significant increases in Si concentrations, in 37% and 23% of European and North American waters, respectively. The median change in Si concentration for the study period was negative for waters in Canada ($-3 \times 10^{-3} \text{ mg L}^{-1} \text{ yr}^{-1}$), while Si in general had increased in the other regions with the largest yearly increases in Estonia ($0.07 \text{ mg L}^{-1} \text{ yr}^{-1}$), the Czech Republic ($0.04 \text{ mg L}^{-1} \text{ yr}^{-1}$), and Fennoscandia ($0.03 \text{ mg L}^{-1} \text{ yr}^{-1}$).

3.2. Prediction of Spatial Variation in Fe Concentration Changes

Using partial least squares analysis with 19 input variables we were able to predict 34% of ΔFe variations across the 340 sites (Table 2). Among the input variables trends in Si and SO_4 concentrations, the percentage of coniferous forest in the catchment, and the site-specific long-term (1960–1990) annual mean air temperature were most influential in explaining variation in ΔFe (Table 2). Changes in OC concentrations over time did not provide significant additional prediction of ΔFe variation across the sites (Table 2). The same variables came out as the most influential when the 110 sites with significant Fe concentrations trends were included in the PLS, and the degree of explained variation increased to 53% (Table 2).

ΔFe was positively related to the percentage of coniferous forest in the catchment area (Figure 4). This pattern was consistent with the geographical distribution of Fe trends, where waters with the strongest increase in Fe concentrations were located in the boreal or hemiboreal region (Figure 2).

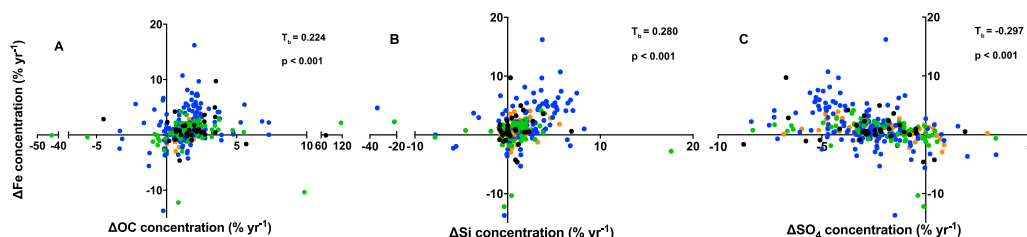


Figure 5. Relationships of relative change in Fe with OC concentration (a) ($N = 314$), (b) Si concentration ($N = 242$), and (c) SO_4 concentration ($N = 313$). T_b is the correlation coefficient Kendall's tau- b . Symbols represent data for headwater streams (black), higher-order streams (green), lakes (blue), and river mouths (orange).

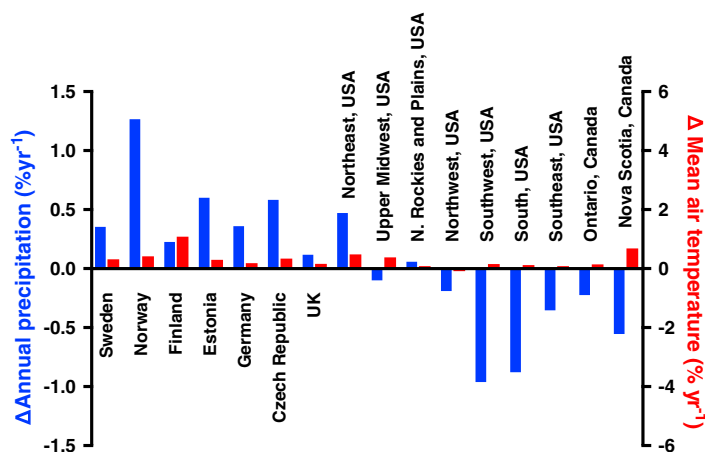


Figure 6. Changes in annual precipitation (left y axis, blue bars) and mean temperature (right y axis, red bars) during 1990–2013 for the countries or climate regions covered in this study.

ΔFe was also positively related to changes in both Si and OC (Kendall's tau, $p < 0.001$ for both OC and Si; Figure 5) but negatively to changes in SO_4 concentrations (Kendall's tau, $p < 0.001$; Figure 5).

Apart from changes in water chemistry, we also examined trends in climatic variables. Trend analyses of long-term climate data (1990–2013) showed a tendency toward increased annual mean air temperature in all the regions included in this study (Figure 6). Changes in annual precipitation were more variable between regions. In northern Europe precipitation has generally increased over the period analyzed, whereas it generally declined in North America (Figure 6).

4. Discussion

Our results demonstrate that Fe concentrations have increased in many northern European freshwaters during the past decades, and in few of the studied North American freshwaters (Figure 2). These results correspond to previous local and regional Fe trend studies that have reported on an increase in Fe concentrations in various freshwaters

(Knorr, 2013; Kritzberg & Ekstrom, 2012; Neal et al., 2008; Sarkkola et al., 2013; Weyhenmeyer et al., 2014). Also, the magnitude of the trends was comparable to those of previous studies. Kritzberg and Ekstrom (2012), for example, found a yearly increase in Fe concentration between 0.5 and 12.3% in river mouths during 1972–2010. For the Swedish sites in our study, including the same river mouths, changes in Fe concentration ranged between -3.4 and 6.4% per year. In Kritzberg and Ekstrom (2012) the highest increase in Fe concentration was found in the southern part of Sweden, which again matches well to our results based on a larger number of Swedish freshwaters (Figure 2).

Rising Fe concentrations have often been associated with increases in dissolved organic matter (DOM) concentrations (Kritzberg & Ekstrom, 2012; Neal et al., 2008; Sarkkola et al., 2013; Weyhenmeyer et al., 2014), which may suggest that the Fe export capacity of the catchment is determined by the availability of DOM as a transporting agent for Fe to aquatic ecosystems. In oxic waters with neutral pH, the interaction between Fe and DOM is a requisite for Fe to stay in suspension (Stumm & Morgan, 1996). Hence, the fact that peatlands and coniferous forests act as important Fe sources (Bjorkvald et al., 2008; Kortelainen et al., 2006) is related to their relatively high DOM concentrations when compared to other types of land cover (Camino-Serrano et al., 2014; Kalbitz et al., 2000). Peatland and forest soils often yield more dissolved Fe than mineral soils, although the latter soil type contains more bound Fe (Dillon & Molot, 1997; Kortelainen et al., 2006; Maranger et al., 2006). The Fe transport capacity is also affected by the organic matter composition, whereby high molecular weight DOM—such as fulvic and humic acids—act as important Fe carriers due to their high affinity for Fe (Laglera & van den Berg, 2009; Riise, 1999).

Given the connection between Fe and DOM, it is logical that Fe concentrations often correlate with DOM in surface waters, both spatially and temporally (Kritzberg & Ekstrom, 2012; Neal et al., 2008; Oni et al., 2013; Sarkkola et al., 2013; Weyhenmeyer et al., 2014), and increasing Fe concentrations are occasionally attributed to increases in DOM concentration (Neal et al., 2008; Sarkkola et al., 2013). Our results support a close Fe-organic matter coupling, since increasing Fe concentrations were paralleled by increasing OC in 77% of our waters, although OC trends did not come out as an important variable in our PLS for the prediction of Fe trends. Three different mechanisms could lead to concurrent trends in Fe and OC: (a) the increase in OC is driving the increase in Fe by enhancing Fe solubility, (b) the increase in Fe is driving the increase in OC by reductive dissolution of Fe and subsequent release of associated OC, and/or (c) the Fe and OC are both responding to one or more other drivers.

For Swedish waters it has been argued that increasing DOM concentrations are unlikely to be the primary driver for observed Fe trends, since Fe:DOM ratios have generally increased, and Fe has increased without a concurrent increase in DOM in several water bodies (Kritzberg & Ekstrom, 2012). If aqueous Fe concentrations were primarily limited by DOM concentrations, Fe and DOM would be expected to increase proportionally. Moreover, experimental additions of Fe to natural waters have demonstrated that DOM has considerable excess capacity for keeping Fe in suspension (Kritzberg, Villanueva, et al., 2014; Kritzberg & Ekstrom, 2012).

A final argument against the importance of increasing DOM as a main driver behind Fe trends is that seasonal dynamics in riverine Fe and DOM concentrations are often not linked (Ekstrom et al., 2016).

Knorr (2013) suggested that reduction of Fe is a major reason for DOM release from soil, rather than DOM being the main regulator of Fe, because reductive dissolution of Fe(III) oxyhydroxides will release coprecipitated and adsorbed DOM. Dissimilatory Fe reduction has been shown to be an important mechanism for Fe dissolution and C release in a controlled incubation experiment and to release more Fe than OC (Pan et al., 2016). This mechanism was suggested to explain increasing Fe and OC concentrations in German streams, where declining N deposition was argued to promote Fe reduction (Musolff et al., 2016). However, this explanation was argued against, since the increase in OC was too large compared to Fe to be explained by this mechanism (Kalbitz, Kaiser, & McDowell, 2017). It should be noted, however, that patterns observed in surface waters may not fully reflect the mobilizing mechanism at the source. For instance, differences in redox conditions and pH in the transition from soil to water may affect Fe and OC transport differently.

In the PLS, relative changes in OC concentration did not come out as an important variable explaining variations in Fe (Table 2). This points to the importance of environmental drivers that affect both aquatic Fe and OC, independently or in concert. Candidate drivers, such as increasing precipitation and consequent hydrological changes, longer growing seasons, and declining sulfate deposition, are discussed in the following sections.

4.1. Hydrological Changes as a Potential Driver for Increasing Fe Concentrations

Differences in precipitation patterns (Figure 6) may partly be the reason for the general difference in Fe trends between the European and North America sites (Figure 2). Increasing precipitation may influence Fe concentrations by enhancing the Fe export from catchment soils (Figure 1). For instance, in Swedish waters, ΔFe was significantly higher in headwater streams than in higher-order streams and river mouths (Figure 3c), although these results need to be interpreted with care due to the small number of headwaters available. The increase in OC and Si in systems with positive Fe trends may indicate that an increase in catchment export contributes to the observed positive Fe trends, since Si and OC mainly originate from catchment soils. Previous studies have shown that Fe concentrations in running waters are following changes in water discharge both seasonally (Mattsson et al., 2017) and on decadal scales (Ekstrom et al., 2016). In Fennoscandia, a simultaneous increase in DOM and Fe in rivers was attributed to increased precipitation, essentially from increased runoff from organic-rich superficial soil layers (Forsberg, 1992).

Simultaneous changes in Fe and Si, and the significance of ΔSi in explaining ΔFe in the PLS model, may be indicative of an increased export from soil layers rich in both Fe and Si, as a factor behind the observed increasing Fe trends. In boreal podzol profiles, Fe and Si are enriched at similar soil depths (Giesler et al., 2000; Riise et al., 2000). Hence, increased flow through intermediate soil depths rich in Fe and Si, due to long-term increases in precipitation and longer growing seasons, has previously been suggested to promote increases in Fe concentrations (Weyhenmeyer et al., 2014). Furthermore, a warmer and wetter climate may enhance weathering rates and groundwater discharge over the year, and result in increased export of weathered minerals such as Si to streams (Smedberg et al., 2006). These processes are relevant for Fe export from mineral soils, and flow patterns could look quite different in peatland and wetland soils (Peralta-Tapia et al., 2015).

Apart from increasing runoff, a wetter climate may result in changes in the groundwater table and soil saturation, with a shift toward more reducing conditions in soils of the catchment areas (Figure 1). By monitoring pore water Knorr et al. (2009, 2013) showed that Fe reduction was favored during periods of elevated groundwater table, which led to increasing Fe and DOM mobilization to a nearby stream. In Swedish rivers, the seasonal Fe variability has been shown to be predominantly driven by the prevalence of reducing conditions in the catchment (Ekstrom et al., 2016). Moreover, Sarkkola et al. (2013) found increasing Fe trends to be particularly pronounced in early winter. This pattern was suggested to be due to increasing winter temperatures and precipitation in the form of rainfall, resulting in anoxic conditions in soils and enhanced mobilization of Fe to receiving water bodies. In contrast, drought and lowering of the groundwater table in wetlands resulted in more oxidizing conditions and a decrease in the release of Fe (Dillon & Molot, 2005; Landre, Watmough, & Dillon, 2009).

Precipitation may also be an important regulator of Fe trends by changing the flushing rate of water through the aquatic conduit (Weyhenmeyer et al., 2014). Sedimentation processes in lakes are strongly dependent on the water flushing through lakes, whereby sedimentation declines at high flushing rates. Considering the significantly higher rate of Fe increase in lakes compared to higher-order streams and river mouths (Figure 3a), a declining efficiency of lakes as Fe sinks is possibly contributing to the observed positive Fe trends.

4.2. Declining Sulfur Deposition as a Potential Driver for Increasing Fe Concentrations

The relationship between ΔFe and relative changes in SO_4 concentrations suggests that declining S deposition in the past few decades may have contributed to the increasing Fe trends (Figure 5). SO_4 was also an influential variable in the PLS (Table 2). The presence of S may have a direct effect on Fe mobility by the formation of stable precipitates with sulfide during reducing conditions in soils and sediment (Figure 1) (Berner, 1984; Davison, 1993). Furthermore, since Fe^{3+} - and SO_4^{2-} -reducing bacteria compete for organic substrates (Chapelle & Lovley, 1992), a reduced input of SO_4^{2-} may favor Fe reduction. Negative relationships between Fe concentrations and SO_4 reduction have been reported across freshwater systems (Nurnberg & Dillon, 1993) and for peat pore water (Bottrell et al., 2007).

The decline in S deposition has been reported as a major factor driving the increasing DOM concentrations in the Northern Hemisphere (Monteith et al., 2007). Hence, the relationship between Fe and SO_4 observed in this study is in line with Neal et al. (2008), who suggested that the observed Fe trends are an indirect effect of the declining S deposition through increasing DOM concentrations. The lower significance in OC trends in explaining ΔFe in the PLS (Table 2), when compared to the direct relationship between S deposition and Fe, however, is not in support of such a mechanism.

A second indirect effect of declining S deposition is the impact on Fe mobility and speciation by altering soil pH. This effect too is highly complex. The solubility of free Fe (Stumm & Morgan, 1996) and the interaction between hydrolyzed Fe and adsorbed organic matter—which promotes solubility—are negatively related with pH (Kalbitz et al., 2000), while the ability of organic matter to complex free Fe ions increases with pH. In this study there was no difference in the distribution of positive and negative Fe trends between low pH systems ($\text{pH} \leq 5$) and medium/high pH systems ($\text{pH} > 5$) (data not shown). Hence, the observed changes in Fe found in this study are not considered to be primarily driven by changes in pH.

Yet another indirect effect of declining S deposition on Fe mobility may occur in soils that have not recovered from acidification. In acidified soils depleted in base cations the release rates of metals such as Al and Fe into the soil water increase to maintain the charge balance (Evans et al., 2008; Lawrence, 2002; Norton et al., 2004). Moreover, an increase in OC in the base cation-depleted soils may further mobilize Al and Fe by complexing the metals.

In conclusion, considering that ΔFe and changes in relative SO_4 concentration were negatively related, the decline in atmospheric S deposition may be a driver behind the increasing Fe trends, although the mechanisms behind this correlation remain unclear. On a regional scale, however, differences in S deposition cannot fully explain differences in the magnitude and frequency of observed Fe trends between North America and Europe. Decreases in SO_4 concentration for the study period were similar across all waters, independently of the region.

4.3. Other Potential Drivers for Increasing Fe Concentrations

Most of the positive trend sites were located in catchments with a relatively high percentage of coniferous forest cover. Presumably, the accumulation of organic soil layers in coniferous forests is a considerable Fe source to receiving waters, since the association with OM facilitates Fe solubility and mobility (Stumm & Morgan, 1996). Moreover, the rather low pH in forest soils may further promote Fe mobilization since the solubility of Fe increases with decreasing pH (Stumm & Morgan, 1996). The recent regrowth of forest, and in particular coniferous forest, at the expense of agriculture has resulted in enhanced vegetation productivity and carbon accumulation in vast regions of both northern Europe and North America (Guo & Gifford, 2002). This has been suggested to be an important mechanism behind increasing DOM concentrations in Swedish freshwaters (Kritzberg, 2017) and may potentially influence Fe trends in these areas too. Furthermore, an increase in vegetation cover—especially of coniferous forest—has been shown to enhance weathering rates of Si and to influence fluxes of both Si and OC to boreal rivers (Humborg et al., 2004).

In addition to land use, Fe and OM dynamics are affected by temperature, which influences the duration of the growing season and watershed hydrology. In a Finnish study, higher Fe concentrations in lakes located in the south than in the north of Finland were linked to a longer ice cover period in the north, resulting in a reduced terrestrial input of Fe (Kortelainen et al., 2013). Furthermore, mean annual air temperature has been shown to have a strong control on aquatic OC concentration for middle- and high-latitude systems with high OC production at intermediate temperatures promoting both litter production and soil wetness with slow mineralization rates (Laudon et al., 2012). This is consistent with a positive correlation between OC and mean air temperature found for numerous Scandinavian lakes (Weyhenmeyer & Karlsson, 2009). In this study, the significance of mean annual air temperature in explaining Fe trends in the PLS model may reflect the potential for accumulation of organic matter in boreal areas, and consequently the mobility of both OC and Fe in coniferous forest soils.

4.4. Trend Implications and Future Projections

Although Fe is an essential element, elevated Fe levels may cause harm to aquatic biota (Vuori, 1995). High concentrations of Fe result in Fe(oxy) hydroxide or Fe-humus precipitates on biological and other surfaces (Peuranen et al., 1994), which may impair oxygen exchange and ion balance in aquatic organisms (Vuori, 1995). Fe also acts as a vector of highly toxic metals such as lead, arsenic, and vanadium, which are reported to increase in Swedish waters (Wallstedt, Bjorkvald, & Gustafsson, 2010). Furthermore, the contribution of Fe to the ongoing browning of waters has been recognized only recently (Kritzberg & Ekstrom, 2012; Weyhenmeyer et al., 2014; Xiao et al., 2015), although the consequences of browning on biota have been highly studied in the past couple of decades. Increasing water color has been shown to affect phytoplankton community composition (Ekvall et al., 2013; Grubisic et al., 2012; Weyhenmeyer, Willen, & Sonesten, 2004), food-web structure (Hansson et al., 2013; Wissel, Boeing, & Ramcharan, 2003), and the biogeochemical role of freshwaters in carbon cycling (Kritzberg, Graneli, et al., 2014).

On the other hand, rising Fe concentrations may reduce P availability by coprecipitating phosphate under oxic conditions in freshwaters. Artificial Fe addition has been used as a restoration measure on lakes suffering from eutrophication (Bakker, Van Donk, & Immers, 2016) and has successfully reduced the phytoplankton abundance and shifted community structure from cyanobacterial dominance to a more diverse community (Orihel et al., 2016).

Although precipitation records are highly variable, large-scale patterns of increasing precipitation in higher latitudes as well as more precipitation falling as rain rather than snow have been identified for much of the Northern Hemisphere in recent decades (Moberg & Jones, 2005; Trenberth, 2011). Moreover, a wetter and warmer climate in the northern Europe (Raisanen & Eklund, 2012) together with increasing runoff in the Northern Hemisphere (Arnell, 1999; Nohara et al., 2006) is predicted for the future. Clearly, it is not changes in precipitation per se, but rather the hydrological responses such as changes in water saturation, runoff, and flushing rates that have the potential to affect Fe dynamics in aquatic ecosystems.

To the extent that the declining S deposition is driving the positive Fe trends they will presumably level off, although actual recovery may be slow due to the S legacy in soils in predominantly organic pools. However, if Fe is increasing in freshwaters due to increasing precipitation and a longer growing season, Fe will presumably continue to rise. The importance of precipitation and S deposition as drivers of the observed Fe trends are likely to vary both on temporal and spatial scales, partly because absolute levels and relative trends of precipitation and S deposition vary across regions and partly because differences in chemical composition and hydrological properties of riparian wetlands and organic and mineral soils imply that the mechanisms that govern the transition of Fe from the source to nearby surface waters may differ. Since Fe is an important player in several global biogeochemical cycles, contributes to the ongoing browning of freshwaters, and is involved in the sequestration of P and C, rising trends in Fe concentrations may have far-reaching implications. Hence, additional studies specifically directed toward understanding the mechanisms driving Fe to increase are imperative. Future work should distinguish between different types of source areas (e.g., wetlands and mineral soils) that likely differ regarding the controls of Fe mobilization and also address the transition between source and surface water to understand to what extent patterns in surface water concentrations are linked to the mobilizing mechanisms.

Acknowledgments

We thank the various environmental monitoring programs and initiatives for collecting the data used in this study. This project was primarily funded by VR (2015-05450) and FORMAS (2015-1407) through funding to E.K. G.W. was supported by the Swedish Research Council (grant 2016-04153), the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement 643052 (C-CASCADES project), and by the Knut and Alice Wallenberg Foundation (KAW project). Chemical analysis of samples from the UK Upland Waters Monitoring Network (C.E. and D.M.) was conducted by the Natural Environment Research Council (NERC) Centre for Ecology and Hydrology laboratories and Marine Scotland Freshwater Laboratories, Pitlochry, under funding from NERC, the Department for Environment and Rural Affairs, and a range of other UK national and devolved government institutes and agencies. M.G. and H-P.G. acknowledge the Leibniz Society for funding the Lake Stechlin long-term monitoring program and the IGB-Neuglobow sampling team. I.K. was supported by the University of Latvia grant AAP2016/B041, and I.K. and J.S. acknowledge Marina Cicendajeva for collecting and managing the Latvian data. P.K., A.R., and J.L. were supported by the Academy of Finland through the TEAQUILA project, decision no. 263476. Collection and analysis of the Krycklan data (H.L.) has been funded by the Swedish Science Foundation (VR) SITES, FORMAS, and SKB. N.L. was supported by the National Science Foundation, DEB-1440297, NTL-LTER. F.O. acknowledges the Czech Science Foundation grant 15-081245. G.R. was supported by the Norwegian University of Life Sciences. J.R. acknowledges the Ontario Ministry of the Environment and Climate Change for funding the data collection. P.N., T.N., and K.K. were supported by the institutional research funding IUT 21-02, and by the target financed project SF170006s08, of the Estonian Ministry of Education and Research. S.S. was supported by the Atlantic Salmon Conservation Foundation and Environmental Canada Acid Rain Monitoring Program. We also acknowledge Reed Green at the U.S. Geological Survey for assisting with the USGS water quality database and two anonymous reviewers for their constructive comments. Raw data sets can be downloaded from the data repository DRYAD, doi:10.5061/dryad.0pn79. This work highly profited from the international network abbreviated as GLEON.

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