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Discussions**

Increasing iron concentrations in surface waters – a factor behind brownification?

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Abstract

Browning of inland waters has been noted over large parts of the Northern Hemisphere and is a phenomenon with both ecological and societal consequences. The increase in water color is generally ascribed to increasing amounts of dissolved organic matter of terrestrial origin. However, oftentimes the increase in water color is larger than that of organic matter, implying that changes in the amount of organic matter alone cannot explain the enhanced water color. Water color is known to be affected also by the quality of organic matter and the prevalence of iron. Here we investigated trends in water color, organic matter and iron between 1972 and 2010 in 30 rivers draining into the Swedish cost, and peformed a laboratory iron addition experiment to natural waters, to evaluate the role of iron and organic matter in determining water color. By comparing the effect of iron additions on water color in the experiment, to variation in water color and iron concentration in the monitoring data, we show that iron can explain a significant share of the variation in water color (on average 25 %), especially in the rivers in the north of Sweden (up to 74 %). Further more, positive trends for iron are seen in 27 of 30 rivers (21–468 %) and the increase in iron is larger than that of organic matter, indicating that iron and organic matter concentrations are controlled by similar but not identical processes. We speculate that increasing iron concentrations can be caused by changes in redox conditions, that mean that more anoxic water with high concentrations of soluble FeII are feeding into the surface waters. More studies are needed about why iron is increasing so strongly, since both causes and consequences are partly different from those of increasing organic matter content.

1 Introduction

It is frequently reported that water color is increasing strongly in many lakes and running waters of the Northern Hemisphere (Driscoll et al., 2003; Frey and Smith, 2005; Monteith et al., 2007; Erlandsson et al., 2008; Haaland et al., 2010). This is a

phenomenon with far reaching ecological and societal consequences as, it is bound to affect the structure and function of the aquatic ecosystem, e.g. through the impaired light climate, and reduce the recreational value and potential to use the water as a drinking water resource (Chow et al., 2007). The drivers behind this trend, sometimes referred to as brownification, are heavily debated and have been ascribed to hydrological factors (Hongve et al., 2004; Erlandsson et al., 2008) as well as an increase in temperature, changes in land-use and reduced acid deposition (Correll et al., 2001; Freeman et al., 2001; Monteith et al., 2007). Although it has been difficult to tease out a single factor causing brownification, there is an implicit consensus that the *direct* factor causing brownification is increased amounts of terrestrially derived organic matter (OM) in the water. This is reasonable, as dissolved OM correlate well with water color (Pace and Cole, 2002; von Einem and Graneli, 2010) and is considered responsible for most of the light absorption in natural waters. Many studies report a concurrent increase in OM content along with the increase in water color, however, water color has often increased significantly more than OM (Hongve et al., 2004; Erlandsson et al., 2008). This suggests that the increase in OM content alone does not suffice to explain the increase in water color.

Apart from the amount of OM, the *quality* of OM (Martin-Mousset et al., 1997) and iron (Fe) are known to affect water color (Pennanen and Frisk, 1984; Maloney et al., 2005). Unfortunately, measures of OM quality are rarely included in environmental monitoring or experiments addressing brownification (but see Freeman et al., 2001; Ekström et al., 2011). By contrast, there is a wealth of studies reporting correlations between Fe and water color (Canfield et al., 1984; Pennanen and Frisk, 1984; Heikkinen and Ihme, 1995; Maloney et al., 2005). Although it is well known that water color is caused by both OM and Fe, few estimates of the interference of Fe with color have been presented (Pennanen and Frisk, 1984) and to our knowledge the potential role of Fe to brownification has not been studied.

In this study we address the direct causes behind brownification across the latitudinal and climatic gradient of Sweden. More specifically, we evaluate the different roles

of OM quantity, OM quality and Fe for water color in 30 rivers during a period of 38 yr. The statistical analysis of this large monitoring dataset is complemented with a laboratory experiment to assess the effect on water color in response to Fe. The main aim is to understand the role of Fe to brownification, as this is imperative for a better understanding of the underlying drivers, but also because increasing amounts of Fe may have partly different consequences to the aquatic system than increasing amounts of organic matter.

2 Material and methods

2.1 Analyses of monitoring data

Data from rivers in the Swedish national monitoring program (run by the Swedish University of Agricultural Sciences) was used. The data is freely available at http://www.ma.slu.se. Rivers with long and continuous time series, or with only minor gaps, of water color, chemical oxygen demand (COD), total organic carbon (TOC), Fe and manganese (Mn) were selected. Rivers that we know to be heavily affected by industrial activities, such as pulp mills, were excluded. This resulted in a dataset with 30 rivers with monthly samples 1972–2010 (Table 1). For one river data was available only from 1976 and five rivers had Fe and Mn data only from 1976 and onwards. Data on TOC was available only from 1987 and onwards. Because data on a few variables were incomplete for 2010, data from 2009 were selected for some inter-comparisons between rivers. Data on export loading, i.e. accounting for the export to the coastal waters by considering both concentrations and water discharge, was available until 2008.

The 30 rivers are located throughout Sweden, between latitude 54°–69° N and longitude 10–24° E and encompass a gradient regarding both climate and vegetation type (Fig. 1). Most of Sweden has a climate dominated by high humidity, cool summers and cold winters with snow (Dfc, according to the Köppen-Geiger climate classification),

and ranges from dry, polar climate in the north (ET) to warm temperate, humid climate, with warm summers in the south (Cfb; Kottek et al., 2006). Most catchments are dominated by boreal vegetation but the vegetation type ranges from alpine in the north, to nemoral in the south. The drainage areas vary in size from 300 to 34 400 km^2, with a mean of 10 400 km^2 and drain into the Bothnian Bay, Bothnian Sea, Baltic proper, Kattegat and Skagerrak (Fig. 1).

Water chemical analyses within the monitoring program were performed using national/international standards and subjected to quality control routines as defined in the accreditation of the laboratory at the Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences. Water color was determined as absorbance of unfiltered water at 420 nm in a 5 cm cuvette (Abs$_{420}$; 5 cm^{-1}). Organic matter content was measured by two methods, COD and TOC. COD was assessed as consumption of KMnO$_4$ in unfiltered water. TOC was measured on unfiltered water by oxidative combustion on a Shimadzu total carbon analyzer. Fe and Mn concentrations were determined by ICP-MS on unfiltered samples that were 0.5 % HNO$_3$.

2.2 Experimental Fe addition

To test how much of absorbance at 420 nm can be attributed to the presence of Fe, additions of FeCl$_3$ were made to water from Motala Ström, Lagan and Lake Holmeshulta from the catchment of Mörrumsån and Lake Lindhultsgölen from the catchment of Lagan. These waters were chosen to reflect the range of pH, TOC and Fe concentrations in the monitoring dataset (Table 2). Before the addition of FeCl$_3$, the water was GF/B-filtered (nominal pore size 2.7 µm) to remove large particles. Water was transferred to 100 ml plankton bottles in brown glass and amended with FeIII using a 0.03 M FeCl$_3$ solution in 0.001 M HCl. Additions were made in triplicate and in six different levels for each water. The largest addition was chosen to include the full range of Fe/TOC ratio in the monitoring dataset. The addition gave a reduction in pH, which was re-adjusted to in situ level (± 0.1 pH unit) by the addition of 0.1 M NaOH. The samples were placed on a shaking table for 24 h. The bottles were removed from the shaking

table and pH was measured again to assure stability. To allow for precipitates to sediment, the bottles were then kept still for 30 min before the absorbance at 420 nm was measured on a Beckman DU800 Coulter Spectrophotometer. TOC concentration before FeCl$_3$ addition was measured using a non-purgable organic carbon method on a Shimadzu TOC-VCHP analyzer, Fe before FeCl$_3$ addition was determined with an ICP-AES Optima 3000 DV (PerkinElmer), while a Hanna HI 991300 was used for the pH measurements.

2.3 Statistical treatment

To detect long-term trends, non-parametric Mann-Kendall tests for trends in time series were used. To estimate the magnitude of a trend that was significant by Mann-Kendall, we used the slope of a linear regression line of yearly mean values over time. Comparison of the relative magnitude of change between different variables was tested by paired t-test. Paired t-test was also used to examine differences in export of organic matter and Fe.

Co-variation between variables among rivers was tested by Pearson correlations of yearly mean values. Casual relationships between variables within rivers were tested by linear regressions including data from all sampling dates unless otherwise stated. Variation in water color within rivers was significantly related to both the amount of organic matter and the Fe concentration in the water. To assess if the relationships were independent of each other, we tested if Fe explained any of the variation in the residuals of the water color – organic matter relationship, i.e. controlling for the variation in water color due to organic matter, and vice versa. The same procedure was followed to test if relationships between Fe and alkalinity were independent of the relationship between Fe and organic matter.

The effect of experimental Fe additions on Abs$_{420}$ was examined by linear regression and differences in the magnitude of the response in different water was examined by analysis of covariance (ANCOVA).

Mann-Kendall tests were performed using an Excel macro, MULTMK/PARTMK, developed by Anders Grimvall and Claudia Libiseller, Linköping University, Sweden, in collaboration with the Swedish University of Agricultural Sciences. All other statistical tests were performed in *PASW Statistics* 18.

3 Results

3.1 Analyses of monitoring data

Water color, COD, TOC, Fe and Mn vary considerably among the rivers (Table 1), while the median pH vary within a rather narrow range of one pH unit close to neutral (6.6–7.6). Strongly colored waters (Abs_{420} $5\,cm^{-1} > 0.20$) occur throughout the north-south gradient, but weakly colored (Abs_{420} $5\,cm^{-1} < 0.10$) waters occur only in the more northern rivers. Water color, COD, TOC, Fe and Mn are all inter-correlated among the rivers, e.g. Pearson correlations between yearly means of all variables from 2009 generate r-values in between 0.52 and 0.97. However, the relationships are generally not 1:1 and the ratios between the different variables, e.g. Abs_{420}/COD and Fe/COD, vary among rivers.

Water color increased in 23 out of 30 rivers during the period 1972–2010 (Fig. 2a). No river exhibited a significant decrease in water color. The increase varies from 22 to 279 %, corresponding to an increase of 0.6–7.6 % per year. The largest increase is seen in the southern rivers while little change is seen in the rivers in central Sweden. The northern rivers generally exhibit a significant increase in water color, although smaller than that of the southern rivers. Figure 3 shows the development over time for three rivers of the northern, central and southern parts of Sweden. There is a tendency that the relative increase in water color has been more pronounced in rivers with higher median values of water color ($r^2 = 0.30$, $p = 0.001$), COD ($r^2 = 0.44$, $p = 0.001$), TOC ($r^2 = 0.33$, $p = 0.001$), Fe ($r^2 = 0.16$, $p = 0.028$) and Mn ($r^2 = 0.49$, $p = 0.000$). However, these relationships have rather low explanatory power (r^2-values

above). Thus overall, an increase in water color is seen in rivers from north to south and in weakly as well as strongly colored rivers.

Observations of increasing water color correspond well to changes in both COD ($r^2 = 0.90$, $p = 0.000$), and Fe ($r^2 = 0.75$, $p = 0.000$) across all rivers (Fig. 4), while there was no relationship with changes in Mn ($r^2 = 0.026$, $p = 0.89$). Mn is not considered in the following analysis. COD has increased in 18 of the 30 rivers by 0.5–3.2 % per year, corresponding to an increase of 17–122 % over the whole period (Figs. 2b and 3d–f). In five rivers water color has increased while COD exhibit no significant trend. Since 1987, 20 rivers exhibit increasing water color (data not shown) and 19 an increase in TOC (Figs. 2c and 3g–i).

Water color increased more than COD across all rivers when comparing the relative rate of change (paired t-test; $t = 5.93$, $p = 0.000$) and Abs$_{420}$/COD increased significantly in 26 rivers by on average 0.6 (0.2–2.0 %) per year (see Figs. 5a and 6a–c). Similarly, water color increased more than TOC ($t = 4.81$, $p = 0.000$) and Abs$_{420}$/TOC increased in 12 rivers 0.8 (0.5–1.1 %). This implies that the increase in organic matter content alone does not suffice to explain the increase in water color. The increase in water color may be partly related to changes in organic matter quality. COD and TOC are both used as measures of organic matter content, but COD reflects both quantity and quality of organic matter (see Discussion). COD increased more than TOC ($t = 4.67$, $p = 0.000$) among rivers and COD/TOC changed significantly in 8 rivers by on average 0.5 (−0.1–0.9 %) per year (Figs. 5b and 6d–f). The latter reflects a change in organic matter quality over time.

Fe has increased significantly in 27 rivers (Fig. 2d) and three examples of Fe over time are shown in Fig. 3j–l. The increase varies from 0.5 to 12.3 % per year, corresponding to 21 to 468 % over the whole period. In all rivers where water color show an increasing trend there is a concurrent increase in Fe, while in four rivers Fe has increased (on average 37 % over the whole period) without a significant increase in water color.

There are positive relationships between water color and COD ($r^2 = 0.504 \pm 0.178$, $p < 0.001$), water color and TOC ($r^2 = 0.180 \pm 0.122$, $p < 0.001$), and water color and Fe ($r^2 = 0.457 \pm 0.193$, $p < 0.001$) in all rivers. Since Fe is associated to organic matter, the relationship between water color and Fe could potentially be dependent on the relationship between water color and organic matter, or vice versa. However, the relationships between water color and organic matter and water color and Fe appear to be independent. The relationship between water color and COD is significant also when controlling for the amount of Fe in the water ($p < 0.001$) and the relationship between water color and TOC is significant when controlling for the variation in Fe in the water ($p < 0.05$) for all rivers but five. Similarly, the relationships between water color and Fe are significant also when controlling for the variation in COD for all rivers ($p < 0.001$) and when controlling for the variation in TOC ($p < 0.001$).

Assuming that Fe is contributing to the variability in water color in these rivers, why is Fe increasing? Since Fe is associated with DOM it could be a result of increasing amounts of DOM. The amount of Fe and organic matter measured as COD co-vary within all rivers, but the explanatory power of these relationships is low, i.e. average $r^2 = 0.31$ (0.01–0.70). Similarly, there are significant relationships between Fe and TOC in all but one river but the explanatory power is low, $r^2 = 0.18$ (0.02–0.48). Fe increased in nine rivers where there is no corresponding increase in organic matter. Moreover, Fe increased relatively more than COD across rivers ($t = 3.58$, $p = 0.001$) and Fe/COD increased in 20 rivers by 1.2 (0.05–3.5 %) per year (Figs. 5c and 6g–i). Hence, although there is a relationship between the amount of organic matter and Fe in the water, this is rather weak, and it is not only the amount of organic matter in the water that controls the amount of Fe.

Since there is a general trend that pH is increasing in the rivers, we also wanted to assess Fe concentrations in relation to acidity changes. Fe concentrations were positively but weakly related to alkalinity in five rivers (mean $r^2 = 0.08$). This relationship disappeared when controlling for the correlation between Fe and COD in two rivers. Hence the weak but significant relationship between Fe and alkalinity in some of the

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rivers is probably not the reflection of a causal relationship, but rather a reflection of the seasonal co-variation of the two factors, and increasing Fe concentrations do not appear related to reduced acidity.

3.2 Export of Fe and organic matter

That concentrations of Fe have increased more than the amount of organic matter in the water is also reflected by the relatively larger increase in the export of Fe to coastal areas compared to that of OM (Table 3). The export of Fe has increased significantly between 1972 and 2008 in the areas that drain into the Bothnian Bay, the Baltic proper, Kattegat and Skagerrak, but not in the area draining into the Bothian Sea. The export of organic matter as measured by COD exhibit a similar pattern, but the increase is smaller ($t = 4.07$, $p < 0.01$) and nonexistent in three areas where there has been a significant increase in Fe (Table 3).

3.3 Experimental Fe addition

Experimental additions of Fe resulted in a linear response in Abs_{420} in all four waters (Fig. 7a, Table 2). The magnitude of the response differed, i.e. there was a significant interaction between the two factors ($F = 14.38$, $p = 0.000$). Abs_{420} increased between 0.0075 and 0.0090 cm^{-1} mg^{-1} Fe added, and the magnitude of the response was higher with higher initial DOC content in the water ($r^2 = 0.99$, $p = 0.009$).

The theoretical contribution of Fe to variation in water color in the rivers was estimated by comparing the slope of the Abs_{420} – Fe relationship in the rivers to that of the experimental Fe addition. The variation in water color between years that could theoretically be explained by Fe varied from 6 to 74 %, based on annual means of Abs_{420} and Fe (Fig. 7b). When including all Abs_{420} and Fe data from each river, i.e. accounting also for the seasonal variation, Fe explained 9–75 % of the variation in water color. Although the slopes of the relationships differed significantly when doing the Fe addition to the four different waters, the estimated contribution of Fe to water color in the rivers

was not strongly affected by the choice of slope. Comparing the fraction of water color that could be explained by Fe using the theoretical 0.0075 and 0.0090 slope, the mean difference was 4 percent units.

4   Discussion

The trend analysis of this dataset, including 30 rivers along a 1800 km N–S gradient in Sweden and monthly data from 1972 to 2010, is in line with previous reports of increasing water color and OM concentrations in freshwaters in Europe, Siberia and North America (Driscoll et al., 2003; Frey and Smith, 2005; Monteith et al., 2007; Erlandsson et al., 2008). This brownification is believed to have fundamental ecological implications as well as societal consequences. The analysis of the current dataset also shows that the increase in water color is too large to be explained by the increase in OM alone. Thus, in addition to increasing amounts of OM there must be a change in the *quality* of the OM or an additional factor that contributes to the increase in water color, and it appears that Fe could play that role in many of these rivers. To fully understand both the causes and consequences of brownification it is necessary to know the direct factor behind it.

4.1   The role of organic matter to water color

A current paradigm suggests that dissolved OM is responsible for most of the light absorption in freshwaters (Williamson et al., 1999) and across the rivers of the current dataset, increases in water color correspond well with changes in OM concentrations (COD and TOC). However, in five rivers water color increased without a concurrent change in COD. Moreover, the relative increase in water color was larger than that of the COD across the whole dataset, and Abs_{420}/COD increased over time in 27 rivers. This illustrates that the increase in water color is not entirely driven by an increase in the quantity of OM. By logical reasoning the mechanisms that have been suggested

as potential drivers of elevated OM export from catchments – climate induced changes in terrestrial production, decomposition and fluvial export, increased OM mobility due to reduced sulfate deposition, and changes in land use – should all bring a concurrent change in OM quality. Unfortunately changes in OM quality are rarely addressed in studies of brownification. The change in Abs_{420}/COD and Abs_{420}/TOC over time seen in most of the rivers means that more light is absorbed for each unit of OM. The carbon specific absorbance (Abs_{420}/TOC) can vary depending on the molecular structure of the organic matter. For example, when comparing DOM in soil water from plots exposed to high versus low acid irrigation, the former had lower carbon specific absorbance, corresponding to lower molecular weight and aromaticity (Ekström et al., 2011). Thus, coupled with an increase in DOM in soil water as a result of lower acidification, there was a change in DOM quality. While the larger increase in water color than in OM content in the Swedish rivers may reflect a change towards larger and more aromatic OM, it cannot be excluded that it is due to a color related factor other than OM quantity and quality. On the other hand, the change in COD/TOC seen in eight rivers is clear evidence of a change in OM quality – for each unit of carbon more permanganate is consumed. The relationship between COD and TOC is not fixed and depend on the number of oxygen atoms per carbon atom required to oxidize different organic molecules, i.e. on OM quality. Moreover, the chemical oxidation of OM by permanganate is incomplete and oxidizes approximately 40 % of the total OM (Wilander, 1988). Thus, the increase in COD/TOC over time reflects a change in OM quality, either that a greater share of the OM is susceptible to chemical oxidation or that the OM present in the water is less oxidized. However, though there are logical reasons and strong indications that there have been changes in OM quality in many of these rivers, the data does not allow for any quantitative conclusions on how this contributes to brownification.

4.2 The role of Fe to water color

To the extent that the increase in water color cannot be explained by changes in the quantity and quality of OM, Fe is a potential source of color. Fe is known to contribute to light absorbance and water color in freshwaters and Fe and water color are often correlated across lakes (Canfield et al., 1984) as they are across the rivers in the current dataset. Some studies indicate that complexes between Fe and OM affect water color more than OM alone (Pennanen and Frisk, 1984; Maloney et al., 2005). Recently, increasing Fe concentrations have been reported for UK upland waters (Neal et al., 2008) and a general increase in stream water Fe concentrations was noted in a dataset with 62 Swedish rivers 1996–2009 (Huser et al., 2011). For the current dataset, Fe increased significantly in 27 out of 30 rivers. On average Fe has doubled over the 38 yr period, but there is a large variation with increases between 21 and 468 %. For all the rivers that exhibit an increase in water color there is a concurrent increase in Fe and there is a strong relationship between water color and Fe within rivers, also when controlling for OM.

The role of Fe and dissolved OM to changes in light absorbance in the UV range in a humic lake was explored by Maloney et al. (2005), both by artificial Fe additions and by oxygenating hypolimnic water with high content of FeII, which then oxidized to FeIII and probably formed complex with DOM. Fe was found to be the more important factor controlling changes in UV absorbance and the results further suggest that Fe should be important also in controlling absorbance in the visual spectra, i.e. water color. Our experiments confirm that water color (Abs_{420}) was enhanced by additions of $FeCl_3$. Furthermore, by relating the slope of the relationship between water color and Fe derived from the experiment to that of the variations in water color and Fe within the rivers, we can see that a considerable share of the inter-annual variation in water color can theoretically be accounted for by iron. On average 25 % of inter-annual variation could be theoretically explained by Fe and it seems to be a more important factor in the north (up to 74 %) that in the south (down to 6 %).

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Upon addition of Fe the response in water color in the experimental waters was significantly higher with higher TOC concentration (0.0075–$0.0090\,\mathrm{cm}^{-1}\,\mathrm{mg}\,\mathrm{Fe}^{-1}$). The difference may be due to the differences in OM quality between the waters. While the experimental waters were only analyzed for Abs_{420}, TOC and Fe concentra-
5 tions, monitoring data verifies that water from the four water bodies sampled differ in Abs_{420}/TOC and COD/TOC, indicating differences in OM quality. It has been demonstrated that visible absorbance increases more for OM extracted with XAD-8 isolates (hydrophobic acids, relatively larger MW) than with XAD-4 (hydrophilic acids, relatively smaller MW; Aiken et al., 1992) with the same amount of Fe (Pullin et al., 2007).
10 In the XAD-8 extracts, but not the XAD-4 extracts, there was a small shift towards higher molecular weight after the addition of Fe, probably reflecting bridging of organic molecules. Thus, molecular weight and absorbance of OM from different waters may be affected differently by the presence of Fe due to differences in chemical structure.

With the aim to improve the conversion of Abs_{420} to TOC Pennanen and Frisk (1984)
15 estimated the role of Fe on water color by statistical modeling including Abs_{420}, TOC and Fe concentrations of the colloidal fraction of water samples from seven sampling stations in three lakes. They found that the absorbance caused by Fe in a water sample could be calculated by the conversion factor $0.025\,\mathrm{cm}^{-1}\,\mathrm{mg}\,\mathrm{Fe}^{-1}$, i.e. a factor 2.7–3.3 times higher than those derived from our experimental Fe additions. While the addition
20 experiment isolates the effect of Fe, the modeled conversion factor may also be affected by factors apart from Fe but contributing to absorbance, such as OM quality. Repeating the modeling exercise by Pennanen and Frisk (1984) with river data from 2009 yield a factor 0.005–0.022 (mean 0.013) $\mathrm{cm}^{-1}\,\mathrm{mg}\,\mathrm{Fe}^{-1}$, depending on which month we select for the model. It is possible that we arrive at lower values than Pennanen
25 and Frisk (1984) because the latter used the colloidal fraction of the samples to derive their relationship, whereas we use the entire OM. If we apply the factor derived by Pennanen and Frisk instead of the ones derived from the Fe addition experiment, on average 61 % of inter-annual variation in water color could be theoretically explained by Fe, more than 100 % in the north and down to 19 % in the south. Compared to the

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modeling approach, the Fe addition gives a conservative estimate of the role of Fe to variation in water color. Hence we are more likely to underestimate than overestimate the importance of Fe.

It appears that in the south, where the increase in color is most pronounced, changes in OM quality, increases in OM quantity and Fe concentration may have contributed to this trend, while in the north Fe may have been more important than changes in OM quantity and quality. The south of Sweden has been more severely affected by sulfur deposition. As reversed acidification has been suggested to be an important factor behind changes in OM quantity (Monteith et al., 2007; Erlandsson et al., 2008) and quality (Ekström et al., 2011), this phenomenon may be more important in the southern part of Sweden, and this may be reflected in the strongly upward trends in the south and few and smaller trends in the north.

4.3 Why is Fe increasing?

In contrast to terrestrial OM export, the mobility of Fe should not be directly enhanced by the reduced acidity of soils since the solubility of FeIII is reduced at higher pH due to the formation of Fe-hydroxides. Landre et al. (2009) found Fe concentrations to be independent of acidity (SO_4^{2-}) in all compartments (e.g. soil layers, upland and wetland draining streams) of a forested catchment in Canada. Neither were Fe concentrations related to alkalinity in soils, ground and streamwater in the Plynlimon catchments in mid-Wales (Neal et al., 2008). In the current dataset, there were few (5) and weak (mean $r^2 = 0.08$) significant and positive relationships between Fe and alkalinity within rivers of the current dataset and we conclude that the positive trends for Fe are not a direct effect of reversed acidification.

Is OM a driver behind increasing Fe? Spatial and temporal association of Fe and OM, in this dataset and many others, may indicate that positive Fe trends are the result of increasing amounts of OM in the water. In fact, Fe is soluble only under anoxic conditions, as FeII, or at strongly acidic pH, and it is the interaction between Fe and OM that maintain Fe in solution under conditions prevailing in these rivers out

of which it would otherwise precipitate (Shapiro, 1966). There is a spatial relationship between Fe and OM measured both as COD and TOC among the rivers. However, the Fe/TOC ratios vary widely from 10 to 219 µg Fe mg^{-1} TOC (annual means for 2009). This suggests that the spatial controls of Fe and OM are similar but not identical and are probably linked to differences in the catchment characteristics such as the influence of peatland and precipitation (Kortelainen et al., 2006). For example, both Fe and dissolved OM export has been shown to be a function of peatland coverage (Dillon and Molot, 1997).

There are also temporal relationships between Fe and OM, i.e. in 18 out of the 27 rivers where Fe shows a positive trend there is a concurrent increase in COD. A similar association was found in catchments in the UK (Neal et al., 2008). However, the relationship between Fe and OM within rivers is generally weak. Most importantly, the observation that Fe per unit of OM is increasing – Fe/COD has increased in 20 of the rivers by on average 50 % – is at odds with the theory that the increase in OM is the driver behind increasing Fe (Neal et al., 2008). If Fe was controlled by the amount of OM in the rivers it should increase proportionately and in all rivers.

The ability of OM to form complexes with Fe is related OM quality, since Fe associates preferentially with high MW OM (Pennanen and Frisk, 1984). However, it appears unlikely that changes in OM quality would explain such a large increase in Fe/COD, up to 133 %. It has been modeled that over 99 % of the Fe in these rivers occur as oxyhydroxide (ferrihydrite, FeOOH; Wällstedt et al., 2010). Dissolved OM is known to bind to the surface of ferrihydrite and stabilize against aggregation by giving the particle surface a net negative charge (Tipping, 1981). To obtain a broad estimate of the importance of this process, Neal et al. (2008) produced an indicate empirical model based on data from rivers of the UK and found that about 5 % of dissolved OM would be bound to ferrihydrite. Even if the conditions prevailing in the Swedish rivers may differ from those in the UK, the concentrations of unbound OM should be in excess relative to those binding to ferrihydrite. In all, it appears that neither increasing OM nor changes in OM quality can be the sole explanations of increasing Fe.

Given that the trend in Fe is not solely the result of OM trends, the question arises if changes in redox conditions, which strongly influences Fe mobility, is a factor behind increasing Fe. The oxic/anoxic boundary in the soil profile is important for the formation of Fe-OM complexes and the location of this layer is connected to fluctuations of the groundwater table and temperature. In River Kiiminkijoki in the boreal region of Finland, Fe/DOC was found to increase during low flow when runoff originated from deeper partly anoxic peat horizons where Fe was enriched (Heikkinen, 1994). The increasing Fe concentrations in the Swedish rivers would be consistent with increased anoxia within organic soils as catchments wet up. Positive trends for temperature, precipitation and runoff across Sweden since 1972 (Hellström and Lindström, 2008) is in line with increasing anoxia in organic soils. While combining water chemistry data with measures of groundwater levels, water flow and temperature is outside the scope of this study, these aspects warrant further research.

4.4 Implications of increasing Fe concentrations

The positive trends for Fe in the rivers reflect higher concentrations of Fe in the freshwater component of the catchments and also increasing export to coastal areas. Besides the obvious effect of increasing water color and reducing light penetration, Fe may affect the biogeochemical cycling of OM, phosphorus and nitrogen. Photooxidation of OM is enhanced by Fe (Minor et al., 2006), and photooxidation in the presence of Fe promotes the formation of sedimenting particles and an associated loss of OM and Fe (Gao and Zepp, 1998; von Wachenfeldt et al., 2008). Also in the absence of photooxidation Fe appears to stimulate the generation of high molecular weight DOM and to induce a shift towards greater molecular weight (Pullin et al., 2007). Thus Fe may augment photooxidation of OM and also enhance the loss of OM from the water column through aggregation and sedimentation. Due to adsorbtion of phosphate to Fe hydroxides and oxides, Fe affects leaching (Dillon and Molot, 1997), sedimentation (Jonsson and Jansson, 1997) and bioavailability of phosphorus (De Haan et al., 1990). As a co-factor in nitrogenase and nitrate reductase, Fe is potentially limiting primary

productivity, nitrate reduction and nitrogen fixation in marine environments. In fact, Fe additions have been shown to stimulate the production of nitrogen fixing cyanobacteria in the Baltic (Stal et al., 1999; Stolte et al., 2006). Finally, increasing concentrations of Fe can have direct and indirect toxic effects on aquatic biota. Precipitation of Fe on fish gills can impair ion regulation and oxygen uptake (Peuranen et al., 1994). Concentrations of toxic metals such as arsenic and vanadium appear to be determined by concentrations of Fe, and are reported to increase in southern Sweden (Wällstedt et al., 2010).

5 Concluding remarks

The majority of Swedish rivers exhibit strong increases in Fe concentrations over the last four decades. This trend is spatially and temporally associated to increasing water color, and the response in water color to Fe additions suggests that Fe may explain a significant share of the browning of river waters. Although Fe is generally correlated to concentrations of OM, Fe is increasing more than OM, indicating that Fe and OM concentrations are controlled by similar, but not identical, processes. The fact that Fe/OM ratios increase may be due to changes in the amounts of anoxic groundwater, rich in FeII, feeding into these river systems. This points to the importance of changing hydrological and redox conditions, that are connected to climate change, as determinants for browning of inland waters and implies that brownification may be a continuous process if predictions of a warmer and wetter climate for the region hold (Räisänen et al., 2004). It is important to better understand to what extent Fe is contributing to enhanced water color, since to the extent that brownification is an effect of decreased sulfur deposition it is likely to level off, and the consequences of increasing concentrations of Fe are in part different from those of increasing OM.

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Interactive Discussion

Table 1. Median values of pH, Abs_{420}, COD, TOC, Fe and Mn in the 30 Swedish rivers between 1987 and 2010.

|	River	pH	Abs_{420} $(5\,cm^{-1})$	COD $(mg\,KMnO_4\,l^{-1})$	TOC $(mg\,l^{-1})$	Fe $(\mu g\,l^{-1})$	Mn $(\mu g\,l^{-1})$
1	Torneälv	6.8	0.15	25	6.0	821	23
2	Kalixälv	6.8	0.14	20	4.7	894	40
3	Råneälv	6.7	0.21	34	7.4	1368	34
4	Luleälv	6.9	0.06	10	2.5	219	21
5	Piteälv	6.8	0.08	15	3.8	379	18
6	Kvistforsen	6.8	0.07	17	4.1	222	18
7	Rickleån	6.7	0.24	54	11.2	592	22
8	Umeälv	7.0	0.08	18	4.1	215	13
9	Öreälv	6.7	0.27	50	10.4	915	31
10	Gideälv	6.6	0.22	46	9.5	690	34
11	Ångermanälven	6.9	0.09	23	5.1	203	18
12	Indalsälven	7.2	0.06	17	4.1	75	8
13	Ljungan	7.2	0.08	25	6.0	136	7
14	Delångersån	6.9	0.08	24	6.0	124	10
15	Ljusne Strömmar	6.9	0.13	31	6.8	275	16
16	Dalälven	7.0	0.16	34	7.2	306	38
17	Nyköpingsån	7.4	0.17	38	10.3	229	56
18	Motala Ström	7.6	0.13	29	7.5	148	54
19	Botorpström	7.2	0.14	40	11.6	155	27
20	Emån	7.0	0.22	49	11.8	603	82
21	Ljungbyån	6.8	0.25	59	13.8	743	70
22	Lyckebyån	6.7	0.37	68	15.9	1715	137
23	Mörrumsån	6.9	0.18	46	11.2	424	91
24	Helgeån	7.1	0.41	68	14.3	1664	110
25	Lagan	6.7	0.29	53	11.3	880	67
26	Nissan	6.7	0.36	63	12.6	1106	75
27	Ätran	7.0	0.24	41	9.1	618	73
28	Bäveån	7.0	0.32	50	10.3	653	45
29	Örekilsälven	6.9	0.30	46	9.3	557	45
30	Enningdalsälven	6.7	0.14	32	7.7	179	16

Table 2. Chemistry of the waters used for the Fe addition experiment and the regression equation with r^2-values for the increase in absorbance in response to Fe addition for the respective waters (visualized in Fig. 7).

Origin of water	pH	DOC (mg l^{-1})	Fe (µg l^{-1})	Abs$_{420}$ (cm^{-1})	Regression slope (cm^{-1} mg Fe^{-1})	r^2
Lake Vättern	7.0	2.9	34	0.006	0.0075	0.98
Lake Holmeshulta	6.7	8.0	143	0.017	0.0080	0.99
River Lagan	6.7	10.5	631	0.037	0.0084	0.99
Lake Lindhultsgöl	6.6	17.2	625	0.109	0.0090	0.99

Table 3. Percent increase in discharge of total organic matter, measured as COD, and Fe in river mouths of the respective counties (shown in Fig. 1) into the different sub-basins between 1972 and 2008. Numbers within brackets show the yearly rate of change in percent.

County	Sub-basin	COD (%)	Fe (%)
BD	Bothnian Bay	30 (0.8)	73 (2.0)
AC	-II-	43 (1.2)	68 (1.9)
AC	Bothnian Sea		
Y	-II-		
X	-II-		
C	Baltic Proper		
AB	-II-		
D	-II-		116 (3.2)
E	-II-		101 (2.8)
H	-II-	86 (2.4)	185 (5.1)
I	-II-		
K	-II-	182 (5.1)	403 (11.2)
M	-II-	206 (5.7)	426 (11.8)
M	The Sound		388 (10.8)
M	Kattegatt	54 (1.5)	173 (4.8)
N	-II-	2 (0.1)	247 (6.9)
O	-II-		
O	Skagerrak	113 (3.1)	108 (3.0)
Sweden total		32 (0.9)	69 (1.9)
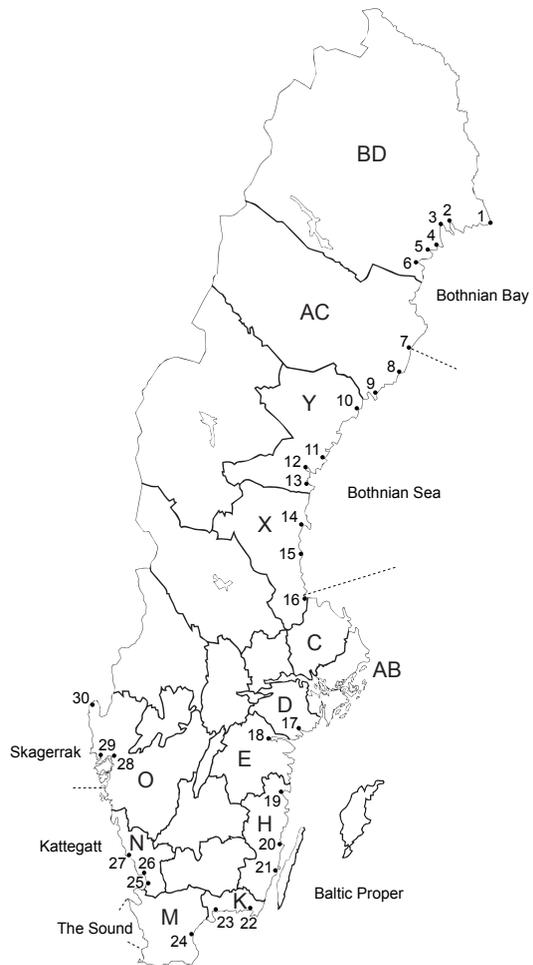
**Fig. 1.** Map of Sweden with the rivers denoted by numbers. Letters denote counties.
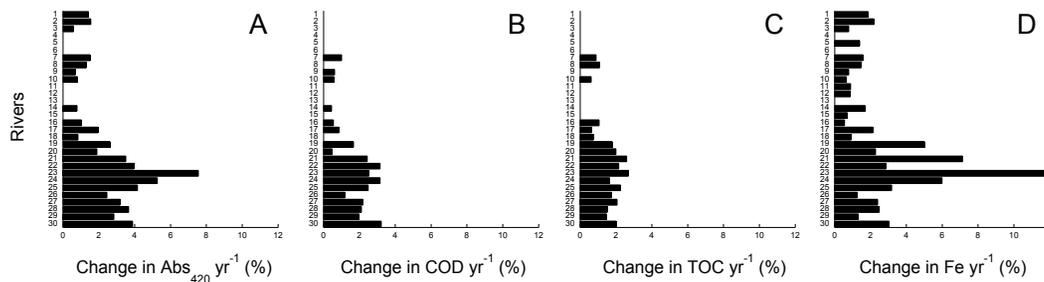
Fig. 2. The rate of change per year of Abs_{420}, COD, TOC and Fe between 1972 and 2010 in all the rivers. When there are no bars there is no significant change over time.
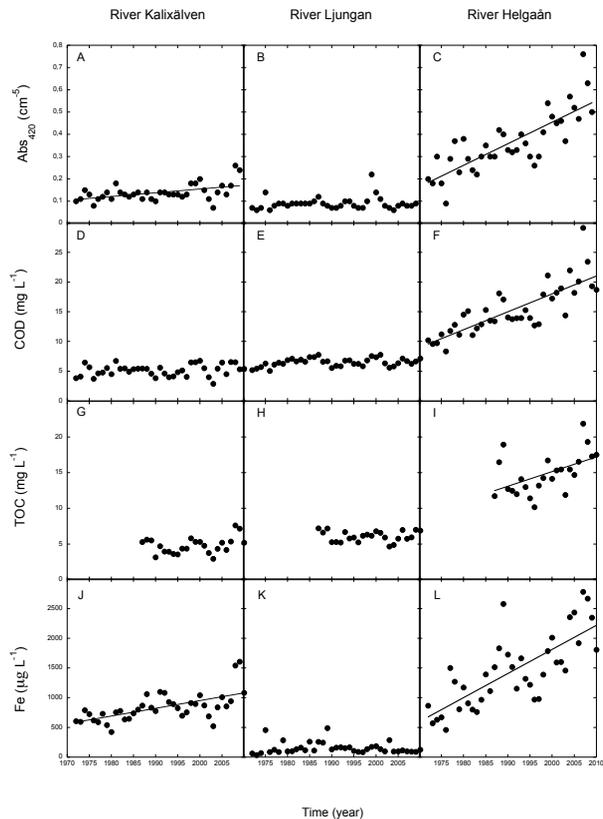
**Fig. 3.** Examples of trends in Abs_{420}, COD, TOC and Fe in rivers in northern (Kalixån), central (Ljungan) and southern Sweden (Helgeån). Trend lines are shown when there are significant increases over time.
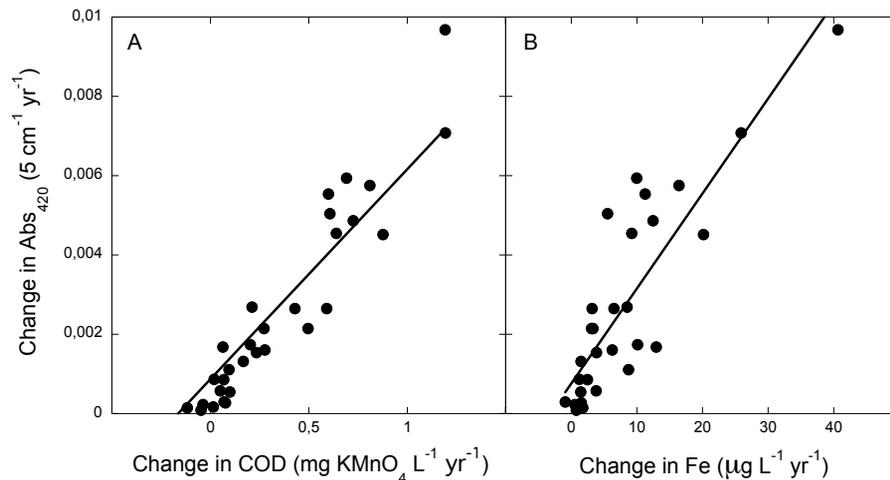
Fig. 4. Changes in Abs_{420} correspond to changes in COD ($Abs_{420} = 0.0064 \times COD + 0.0004$, $r^2 = 0.90$, $p < 0.001$, **(A)** and Fe ($Abs_{420} = 0.0002 \times Fe + 0.0008$, $r^2 = 0.75$, $p < 0.001$, **(B)**.
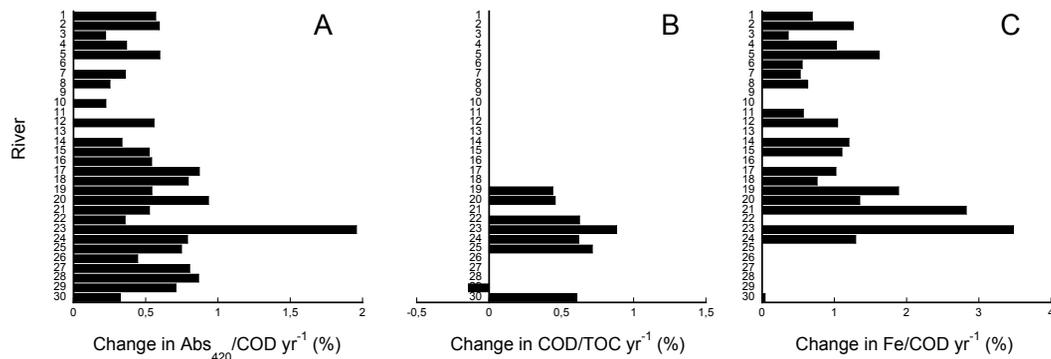
Fig. 5. The rate of change per year of Abs_{420}/COD, COD/TOC and Fe/COD between 1972 and 2010 in all the rivers. Where there are no bars there is no significant change over time.
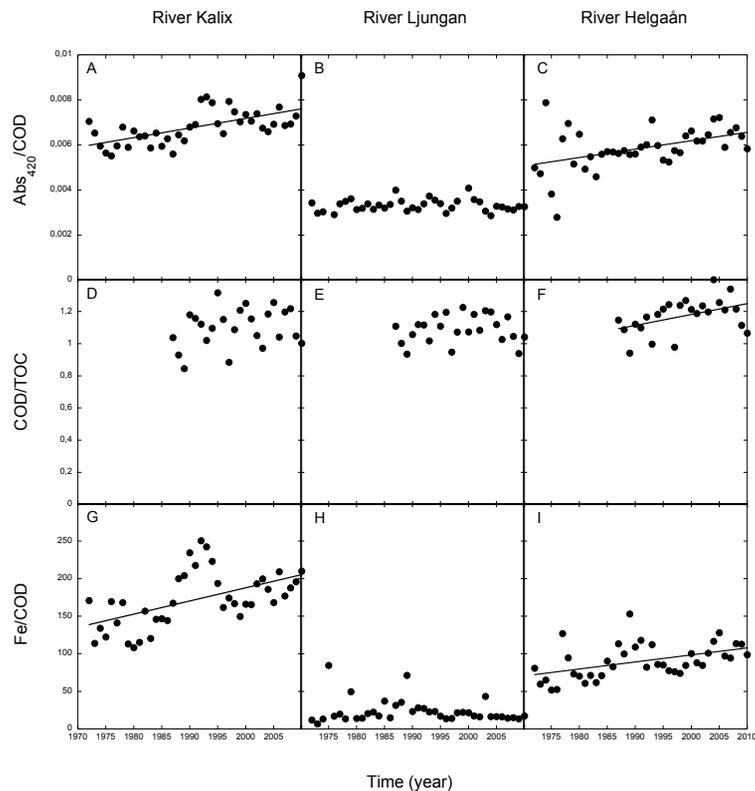
Fig. 6. Trends in Abs_{420}/COD, COD/TOC and Fe/COD in rivers in northern (Kalixån), central (Ljungan) and southern Sweden (Helgeån). Trend lines are shown when there are significant increases over time.
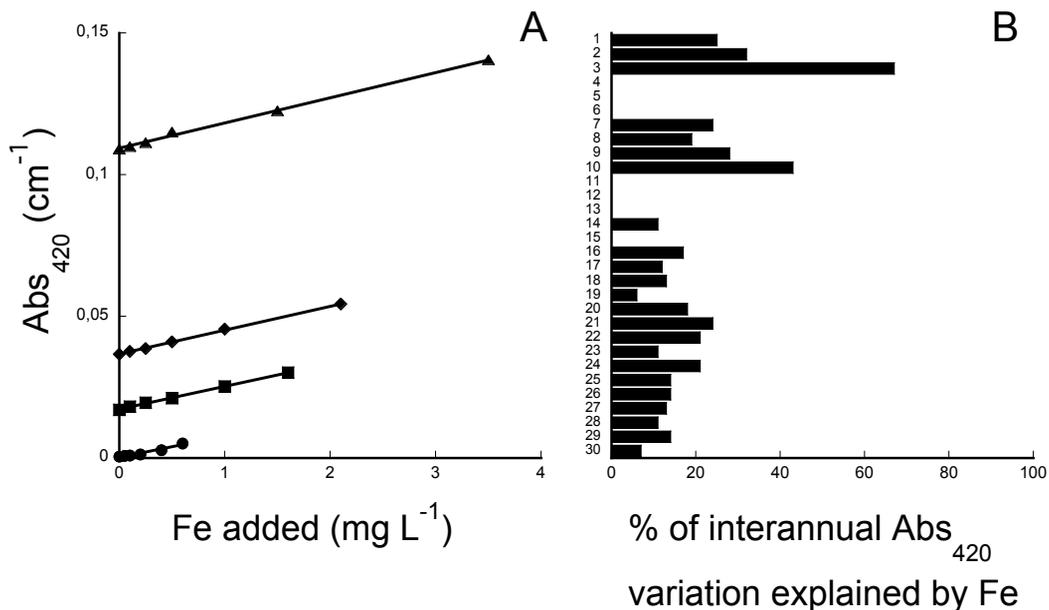
Fig. 7. The theoretical contribution of Fe to Abs_{420}. **(A)** shows the effect of Fe additions on water color as measured by Abs_{420} in water from Lake Lindhultsgöl (▲), River Lagan (♦), Lake Holmeshultasjön (■) and River Motala Ström (•) respectively. All regressions are significant ($p < 0.001$). The slope and r^2 of the regression equations and water chemistry of the different waters are shown in Table 2. **(B)** shows how much of the inter-annual variation in Abs_{420} that could theoretically be explained by variation in Fe for each river. This fraction is calculated by comparing the slope of the Abs_{420} – Fe relationship in each river to that of the experimental Fe addition (the mean of the four slopes derived from the experiment, $0.0083\,\mathrm{cm}^{-1}\,\mathrm{mg}\,\mathrm{Fe}^{-1}$).