



Four decades of changing dissolved organic matter quality and stoichiometry in a Swedish forest stream

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Abstract Dissolved organic matter (DOM) concentrations have risen by a factor of two or more across much of Europe and North America during recent decades. These increases have affected the carbon cycle, light regime, drinking water treatability, and the energy and nutrient budgets of lakes and streams. However, while trends in DOM quantity are well characterised, information on how/whether qualitative properties of DOM have changed are scarce. Here,

we describe over 40 years of monitoring data from a forested headwater stream in the Gårdsjön experimental catchment, southwest Sweden, which provides a unique record of biogeochemical change, including optical and stoichiometric DOM quality metrics, spanning the entire period of recovery from acidification. For the period 1980–2020 we find a 71% reduction in decadal mean sulphate concentrations, and a similar reduction in inorganic aluminium concentrations, alongside a 64% increase in dissolved organic carbon (DOC) concentrations. Over the same period, colour (absorbance at 420 nm) increased almost twice as much as DOC, whereas dissolved organic nitrogen (DON) increased by only one third as much. These results demonstrate a shift in stream water composition, with DOM becoming dominated by highly coloured, complex, nitrogen-poor compounds. This material is likely more resistant to biological degradation, but more susceptible to photochemical degradation. Changes in DOM stoichiometry could lead to intensified nitrogen and/or phosphorus limitation in surface waters, while increased colour/DOC ratios could intensify light-limitation of primary production beyond that expected from DOC increases alone. We observed increases in organic matter associated metals (iron 117%, organically complexed aluminium 85%) that exceeded the increase in DOC, consistent with their increased mobilisation by more aromatic organic matter. All observed changes are consistent with recovery from acidification being the primary driver of change, implying that past acidification, and

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ongoing recovery, have profoundly affected terrestrial and aquatic biogeochemistry, ecology and the carbon cycle.

Keywords Dissolved organic matter · Aquatic carbon · Forest catchments · Stoichiometry · Long-term · biogeochemical trends

Introduction

Dissolved organic matter (DOM) is a key source of energy and nutrients in terrestrial and aquatic ecosystems. Produced through incomplete decomposition of plant and soil organic matter, it tends to be most concentrated in warm, wet organic soils, from which it can be exported to headwater streams, lakes and ultimately the oceans. Throughout this aquatic continuum, DOM is a key component of biogeochemical environments, exerting a strong influence on the composition and function of aquatic ecosystems (Xenopoulos et al. 2017). DOM comprises a wide range of compounds, ranging from simple low molecular weight plant- and microbially-derived compounds through to high molecular weight, complex compounds with a high proportion of aromatic structures. The variable molecular composition of DOM, referred to here as DOM quality, is reflected in its optical properties, elemental composition, and its potential to be an energy source for biological uptake. For example, simple low molecular weight compounds tend to be rapidly metabolised (Berggren and del Giorgio 2015), whereas complex ore aromatic compounds tend to be resistant to biodegradation on timescales of months to years, but are more susceptible to photodegradation (Berggren et al. 2018; Fovet et al. 2020; Li et al. 2020). The elemental composition of DOM varies according to source and subsequent processing, but typically comprises around 50% carbon (C) by weight, and is quantified by the analysis of dissolved organic carbon (DOC), where the dissolved fraction is typically considered to be that which passes through a 0.45 µm filter (Zsolnay 2003). DOM also contains variable proportions of macronutrients, notably nitrogen (N) and phosphorus (P), and can transport metals such as iron (Fe) and aluminium (Al) via complexation (Tipping 2002; Yates et al. 2019). DOM can therefore act as a vector for C,

other nutrients, metals and energy transport within the soil, and through soils to inland waters. Many DOM compounds are chromophoric, and absorb light energy, giving a brown colouration. Thus, high DOM concentrations can have a strong influence on the light regime of many aquatic ecosystems, for example, determining the photic depth of lakes and thus the depth to which aquatic macrophytes and phytoplankton can grow (Sheldon and Boylen 1977; Reitsema et al. 2018). The bioavailable fraction of DOM (which may include compounds formed during photolysis) contributes to bacterial heterotrophic processes, and can therefore affect aquatic carbon and nutrient cycling and ecosystem trophic state (Stutter et al. 2018; Graeber et al. 2021; Rulli et al. 2022). Depending on the biological and photochemical reactivity of the DOM, environmental conditions and residence time of water within the freshwater system, DOM exported from terrestrial systems may be mineralised to CO₂, buried in particulate form in sediments, or exported to marine ecosystems (Cole et al. 2007; Tranvik et al. 2009; Evans, et al. 2017; Williamson et al. 2021). Binding of metals by DOM can increase their transport from soils to waters, but can also reduce their toxicity, notably in the case of Al (Gensemer and Playle 1999).

Over the last several decades, mean and peak concentrations of DOC have increased markedly (in some cases by a factor of two or more) in headwater lakes and streams in many regions of Europe including Fennoscandia, the British Isles and Central Europe, and also in the Northeastern United States and Eastern Canada (e.g. Monteith et al. 2007, 2023; de Wit et al. 2021). While such increases are by no means ubiquitous across all regions and waterbody types, some studies suggest that trends in headwaters have extended into some larger rivers systems, and led to an increased DOC flux from land to sea (Worrall and Burt 2007; Kritzberg and Ekström, 2012; Frigstad et al. 2023). Since their detection in the late 1990s and early 2000s, headwater DOC increases have been variously attributed to climatic changes such as increasing temperatures and higher runoff, increases in atmospheric CO₂ concentrations and nitrogen deposition, and land-use changes such as forest expansion, peatland drainage and the use of fire for upland management (e.g. Porcal et al. 2009; Yallop et al. 2010; Haaland et al. 2010; Škerlep et al. 2020; Nieminen et al. 2021). However, regional and

continental synthesis studies have allowed most of these explanations to be excluded over larger scales, and consistently indicate that recovery from acidification is the dominant driver of DOC increases (Monteith et al. 2007, 2023; SanClements et al. 2012; de Wit et al. 2021; Eklöf et al. 2021, Lawrence and Roy 2021; Redden et al. 2021; Hall et al. 2021). This recovery is the result of major continental-scale reductions in sulphur emissions and deposition, which have taken place in all regions where DOC increases have been observed. The mechanism for this relationship appears to be primarily abiotic and based on solubility; most terrestrially-derived DOC tends to be low-solubility hydrophobic and phenolic compounds (Qualls and Haines 1991) and high levels of acidity and ionic strength in soil pore waters thus suppress concentrations of these weak organic acids (Kalbitz et al. 2000; Hruška et al. 2003; Monteith et al. 2007; Moldan et al. 2012). An abiotic control on organic matter solubility and consequent DOC export has also been supported by core, plot- and catchment-scale manipulation experiments (Clark et al. 2012; Ekström et al. 2011; Evans et al. 2012; SanClements et al. 2018; Cincotta et al. 2019). The most recent large-scale analysis by de Wit et al. (2021) suggests that, despite pollutant sulphur and chloride deposition having declined to very low levels across much of Europe and North America, this mechanism continues to explain the majority of change in DOC to date.

While the evidence for rising concentrations of DOC (and overall dissolved organic matter, DOM) is clear, the evidence for associated changes in the quality of DOM is more limited, and equivocal. Water colour (measured as absorbance over a range of ultraviolet and visible wavelengths) has been used as a direct DOC proxy in many studies, (e.g. Worrall and Burt 2004; Škerlep et al. 2020) implying a stable ratio of absorbance to DOC, but this may not be the case if changes in (for example) organic matter solubility lead to changes in the molecular composition of the leached DOC pool (e.g. Wallage and Holden 2010). In general, a higher ratio of absorbance to DOC (typically characterised as the specific ultra-violet absorbance, SUVA, for a given wavelength) is indicative of a higher proportion of weakly soluble, higher molecular weight, aromatic compounds (e.g. Weishaar et al. 2003). According to the acidification hypothesis, absorbance/DOC

ratios would be expected to decrease along with DOC during the acidification phase, due to the preferential retention of less soluble coloured aromatic DOM, and to increase during the recovery phase. In apparent contradiction of this expectation, Dawson et al. (2009) reported a decrease in the ratio of absorbance at 250 nm to DOC ($SUVA_{250}$) from 1986 to 2008 at a set of Scottish monitoring streams. On the other hand, Stetler et al. (2021) report long-term increases in DOC, absorbance at 440 nm (Abs_{440}) and the Abs_{440}/DOC ratio in 16 of 28 monitored lakes in the Adirondack Mountains, New York, from 1994 to 2012. Similarly, Xiao and Riise (2021) reported an increase in $SUVA_{254}$ in lakes in Southeast Norway, while Oni et al. (2013) reported larger increases in Abs_{420} versus DOC at streams in Northern Sweden. More recently, in an analysis of 92 lakes in eastern Canada, Rodríguez-Cardona et al (2023) reported mostly positive trends in DOC and Abs_{440} , but noted that the two variables were generally uncoupled, suggesting changes in DOM quality. In general, there are few long-term studies in which both DOC and absorbance have been reported, making it difficult to determine whether consistent qualitative changes in DOM are occurring.

Along with the direct biogeochemical and ecological impacts of rising aquatic DOC, indirect effects may occur via changes to the mobilisation of other elements, including nutrients such as nitrogen (N) and metals such as Fe and Al. Of these, N is an intrinsic component of most organic molecules, quantified as dissolved organic nitrogen (DON). Previous work has shown that DOC/DON ratios tend to be lowest in catchments influenced by human activities such as agriculture and urbanisation and highest in catchments draining nutrient-poor organic soils such as peatlands (Wymore et al. 2021). Since more aromatic molecules are weakly acidic and tend to have a high C/N ratio (Yates et al. 2019), increases in organic matter solubility associated with recovery from acidification would be expected to result in an increase in the C/N ratio of the overall aquatic DOM pool. Thus, we would expect trends in DON to be less pronounced than trends in DOC. However, DON is less widely monitored than DOC, and as it is typically calculated as the difference between total and inorganic fractions it is also prone to higher analytical uncertainty. As a result, evidence of long-term trends in DON is limited. For forest monitoring plots in

Flanders, Belgium, Verstraeten et al. (2016) observed increases in soil solution concentrations of both DOC and DON, coinciding with a decrease in acid deposition, but also observed a decrease in DOC/DON ratio. Rodriguez-Cardona et al. (2022) analysed long-term (8 to 45 year) data from 74 streams spanning an Arctic to tropical gradient in the US, Puerto Rico and Finland, and found significant increases in DOC at 43% of sites, and in DON at 30% of sites, while significant decreases were observed at 18% and 19%, respectively. Sites with DOC and DON increases tended to be those recovering from acid deposition, although this was not always the case. DOC/DON ratios were found to have increased significantly at 29% of sites, and decreased significantly at 11%. The authors concluded that DOC and DON were at least partly coupled, and that stoichiometric changes in DOC/DON ratio could alter the energy and nutrient balances of aquatic ecosystems.

Iron concentrations have increased in headwater lakes and streams in the UK (Neal et al. 2008), in headwaters and some larger rivers in Sweden (Kritzberg and Ekström, 2012; Temnerud et al. 2014; Škerlep et al. 2023), more generally in surface waters across large parts of Northern Europe (Björnerås et al. 2017) and in Nova Scotia, Atlantic Canada (Redden et al. 2021). All of these studies have noted a general correspondence between water bodies in which Fe has increased, and those in which DOC has increased. For example, in Sweden Fe, DOC and also Abs_{440} (which can be influenced by both DOC and Fe) follow a clear latitudinal gradient with strong increases in the south and little or no change in the north (Kritzberg and Ekström, 2012). This clearly suggests that the trends may be linked, and therefore potentially associated with the decrease in acid deposition affecting the same regions. Neal et al. (2008) used the WHAM metal speciation model to infer that most Fe in the surface waters studied was present as colloidal Fe(III) oxyhydroxides, and that increases might be due to stabilisation against aggregation by binding of DOM to particle surfaces. Redden et al. (2021) reached a similar conclusion, supported by evidence from size exclusion chromatography showing most Fe to be present in either small (DOM-bound) or large (oxyhydroxide) fractions. Škerlep et al. (2023) observed that tightly coupled increases in Fe and DOC in both riparian porewaters and headwater

streams in forested catchments in Northern Sweden, associated with the formation of mobile organic Fe complexes. However, Kritzberg and Ekström (2012) concluded that Fe and DOC trends were at least partly decoupled, on the basis that DOC was present in excess in Swedish surface waters and therefore unlikely to limit Fe solubility, while Fe/DOC ratios were observed to have increased. On this basis they concluded that Fe increases might be influenced by catchment hydrological conditions, with greater leaching of soluble Fe(II) under wetter conditions. Björnerås et al. (2017) suggested that any link between Fe and DOC might be indirect, for example via independent effects of declining sulphate deposition on organic matter solubility and the soil redox environment. However, a subsequent study by Björnerås et al. (2022) argued against a mechanistic link between the S and Fe cycles based on analysis of lake sediment cores, despite Fe concentrations in both the water column and sediment cores having increased over the period of declining S deposition. The authors instead attributed these increases to changes in land-use and climate.

In general, surface water concentrations of inorganic Al (Al_{inorg}) have tended to track the acid deposition peak, with high levels of acidity mobilising and leaching Al from mineral soils, leading to a range of negative environmental impacts including fish kills (e.g. Cronan and Schofield 1979; Gensemer and Playle 1999). A proportion of Al mobilised from the soil may be organically complexed in the presence of DOM, reducing both its toxicity and solubility (Al compounds can be used as flocculants to remove DOM in water treatment processes; Matilainen et al. 2010). However, a proportion of organic Al (Al_{org}) can remain in solution and be leached to surface waters. Given the multiple influences on Al_{org} , concentrations can be highly variable both spatially and temporally. Long-term trends in response to declining acid deposition are particularly hard to predict, because decreasing soil acidity can be expected to reduce total Al mobilisation, whereas rising DOC concentrations may increase the proportion of that Al which is in an organically complexed form. In surface waters with very high DOC concentrations, this mechanism may even lead to rising total Al concentrations in response to declining acid deposition (e.g. Redden et al. 2021).

Based on mechanistic understanding, we hypothesise that rising DOC concentrations in surface

waters resulting from decreasing acid deposition will be accompanied by a suite of changes in DOM composition and organic matter associated elements including: (1) an increase in absorbance/DOC ratio; (2) a decrease in the DON/DOC ratio; (3) an increase in Fe and (4) an increase in organically bound Al. Collectively these changes have the potential to profoundly alter the status and functioning of aquatic ecosystems, but as noted above the empirical evidence that they are occurring remains weak, and partly contradictory. Here, we evaluate these hypotheses with an analysis of long-term changes in DOM-related metrics in a headwater stream at Gårdsjön, southwest Sweden, which has been monitored since the late 1970s. This unique dataset, which has not been reported in full previously, provides some of the longest and most comprehensive records of DOM-related biogeochemical change, for an area that has undergone some of the most severe freshwater acidification and subsequent recovery in Europe.

Methods

The Gårdsjön research catchment is located in the Bohuslän region of southwest Sweden, north of Göteborg (Gothenburg) (58° 04' N, 12° 03' E) (Andersson and Olsson 1985; Hultberg and Skeffington 1997; Moldan et al. 2012, 2018). Lake Gårdsjön is at an elevation of 114 m, 12 km from the Swedish west coast. Acidic gneissic bedrock is overlain by podzolic soils with a thick humus layer, and the area is largely forested by Norway spruce (*Picea abies* (L.) Karst.) with some Scots pine (*Pinus sylvestris*). The area was established as a research catchment in the late 1970s, with several subcatchments around the lake subject to a range of manipulations including sulphur and nitrogen application, liming, application of clean rain beneath a below-canopy roof, and hydrological manipulation (Hultberg and Skeffington 1997). As part of the overall programme, one subcatchment, F1, was established as the unmanipulated 'reference' catchment, and has been continuously monitored for water quality since 1979. Sampling frequency over the monitoring period has varied between weekly, twice a month and monthly, but without any biases towards particular seasons or hydrological states. Discharge has been measured at the catchment outlet

over the same period using a v-notch weir and water level recorder. The F1 catchment, which is part of the Swedish ICP Integrated Monitoring programme, has an area of 3.7 ha, and an elevation range of 114 to 140 m (Hultberg 1985). It is completely forested with mature (~150 year old) Norway Spruce, with podzolic soils on hillslopes and small peaty *Sphagnum* wetland areas in depressions, which occupy <10% of the catchment area. The long-term mean annual temperature is 6.7 °C, mean annual precipitation is 1000 mm, and mean annual runoff is 520 mm. Snowfall during winter is sporadic and rarely leads to extended periods of accumulation or to snowmelt-driven high flows. Over the last 60 years, southwest Sweden has experienced an increase in average rainfall, and an increase in temperature of around 1 °C, leading to higher average runoff in winter but lower runoff in spring, with no significant trend in flows an annual scale (Teutschbein et al. 2022). Discharge at the F1 catchment has shown a tendency towards higher peak flows during the last 10–20 years, but little change in average discharge (F. Moldan, unpublished data).

Chemical analysis of samples was carried out at the IVL Swedish Environmental Research Institute and the Swedish University of Agricultural Sciences using routine accredited methods (Andersson and Olsson 1985; Löfgren et al. 2011). Briefly, pH was determined by glass electrode, sulphate (SO_4^{2-}) and nitrate (NO_3^-) by ion chromatography, and DOC by thermal oxidation. DON was determined as NH_4^+ following Kjeldahl digestion; NH_4^+ was measured colorimetrically by flow injection analysis, and DON was calculated as the difference between digested and undigested samples. Total Al (Al_{tot}) and Fe were determined by ICP-OES (Inductive Coupled Plasma-Optical Emission Spectrometry); Al_{org} was defined as the fraction of total Al passing through an ion-exchange column, with Al_{inorg} calculated as $\text{Al}_{\text{tot}} - \text{Al}_{\text{org}}$. Over the monitoring period, some analytical procedures changed. Whenever this occurred, both procedures were run in parallel for a period of time and investigations were carried out to ensure data comparability. From 2009 onwards, laboratory data were reported with limits of quantification (LOQ) instead of previously used limits of detection (LOD). Measured values below the LOQ/LOD were set to half of the LOQ/LOD. LOQs used were Fe 0.01 mg l⁻¹, Al 0.05 mg l⁻¹, DOC 0.5–1 mg l⁻¹, NO_3^- 0.005

mg N l⁻¹, NH₄⁺ 0.01 mg N l⁻¹, SO₄²⁻ 0.01 mg S l⁻¹ and total P 0.003 mg P l⁻¹.

A consistent time series of measured light absorbance at 400 nm (Abs₄₀₀) was obtained as follows. Prior to 2015, absorbance was reported as colour in units mg Pt l⁻¹, to maintain continuity with historical colour measurements (when the colour of water samples was determined by comparing the sample to standard solutions of platinum cobalt chloride). To convert absorbance measurements into mg Pt l⁻¹, calibration curves were created by measuring spectrophotometrically the absorbance (400 nm, 1 cm cuvette) of standard solutions of platinum cobalt chloride, then measuring the absorbance of the water sample, and calculating the corresponding value in mg Pt l⁻¹. A calibration curve was created for each batch of samples. If the calibration curve was more than marginally different from the expected theoretical values, the instrument and standard solutions were checked, and a new curve established, which resulted in highly consistent calibration curves over time. For earlier data where the original Abs₄₀₀ values were not recorded, we converted colour in mg Pt l⁻¹ back to absorbance units using a single average calibration curve derived from 69 individual calibration sets provided by the laboratory. From 2015 onwards, Abs₄₀₀ was measured and reported directly.

To analyse qualitative changes in DOM and associated metals we expressed all determinands relative to DOC on a mass basis. For DON this reverses the conventionally used DOC/DON ratio, but allows comparison with other metrics.

Non-marine sulphate (xSO₄²⁻) can be considered a measure of the pollutant-derived fraction of total sulphate leaching, assuming geological sources of sulphur are negligible. This was calculated by adjusting total measured sulphate for the marine component, based on the ratio of sulphate to chloride in seawater.

To estimate long-term changes in solute concentrations, while accounting for variations in sampling frequency and missing values, we calculated mean concentrations for each month during each decade of the monitoring period (i.e. 1980s to 2010s). Decadal mean concentrations were calculated as the mean of the monthly values. The total number of samples per decade was 198 in the 1980s, 238 in the 1990s, 200 in the 2000s and 142 in the 2010s. Mean

solute concentrations and UV absorbance for the month in each year with the lowest and highest values (which varied by solute) were used as an indicator of changes in minimum and maximum concentrations, while limiting the impact of individual outliers. We also ran the non-parametric Mann–Kendall trend analysis method on annual mean values of each determinand using MAKESENS 1.0 (Salmi et al. 2002). The same software was also used to calculate annual average rates of change, along with 95% confidence intervals, based on the Sen slope method.

Results

Decadal mean concentrations of selected chemical determinands are shown in Table 1, while Mann–Kendall trend statistics are shown in Table 2. The majority of measured determinands showed highly significant ($p < 0.001$) trends over the 41-year period; xSO₄²⁻, H⁺, Al_{tot}, and Al_{inorg} all decreased, whereas DOC, Abs₄₀₀, DON, Fe and Al_{org} all increased. The only determinands that did not change significantly were P_{tot} and NO₃⁻.

Based on the time series data, the main driver of historic acidification at Gårdsjon, xSO₄²⁻ appears to have peaked in the F1 catchment shortly after the onset of monitoring, during the mid-1980s (Fig. 1), coinciding with the regional peak of sulphur deposition. Concentrations fell rapidly during the 1990s and have now reached very low levels, with concentrations fluctuating seasonally around a mean of 0.62 (standard deviation of monthly mean values ± 0.31) mg S l⁻¹ in the 2010s, 85% lower than the 1980s mean. Negative concentrations of xSO₄²⁻ (i.e. when the estimated level of marine-derived SO₄²⁻ exceeded measured SO₄²⁻) were recorded during six spring–summer periods since 2005, while large spikes of high xSO₄²⁻ throughout the record almost always occurred during August–October. Stream H⁺ concentrations showed a corresponding and largely monotonic reduction over the same period, again with the most rapid changes in the 1990s, but with a smaller overall reduction in average concentrations of 44%. The changes correspond to a decadal mean pH increase from 4.15 (± 0.04) in the 1980s to 4.40 (± 0.05) in the 2010s. Decadal mean concentrations of Al_{inorg} decreased by 78% over the monitoring period, in line

Table 1 Decadal mean and mean highest and lowest monthly concentrations for selected chemical variables

Decade	Non-marine sulphate mg S l ⁻¹	H ⁺ μeq l ⁻¹	DOC mg l ⁻¹	DON mg l ⁻¹	Abs ₄₀₀ m ⁻¹	Fe mg l ⁻¹	Al _{tot} mg l ⁻¹	Al _{inorganic} mg l ⁻¹	Al _{organic} mg l ⁻¹	Abs ₄₀₀ /DOC l mg ⁻¹ m ⁻¹	DON/DOC mg mg ⁻¹	Fe/DOC mg mg ⁻¹	Al _{organic} /DOC mg mg ⁻¹
Mean	3.98	70.9	9.08	0.24	3.68	0.31	0.97	0.71	0.25	0.40	0.027	0.033	0.028
1980s	3.09	68.9	10.17	0.24	4.30	0.31	0.94	0.62	0.32	0.42	0.024	0.030	0.032
2000s	1.30	50.2	12.77	0.28	6.41	0.54	0.70	0.30	0.41	0.50	0.022	0.042	0.032
2010s	0.62	39.6	14.90	0.29	8.06	0.67	0.63	0.16	0.47	0.53	0.020	0.044	0.032
Lowest month	3.31	61.5	7.14	0.19	2.42	0.19	0.71	0.54	0.18	0.33	0.029	0.026	0.020
1990s	2.45	57.7	7.87	0.19	3.13	0.19	0.69	0.45	0.23	0.38	0.027	0.024	0.026
2000s	0.65	42.2	9.81	0.23	4.77	0.35	0.57	0.24	0.32	0.41	0.025	0.028	0.029
2010s	0.21	33.2	9.22	0.19	4.05	0.38	0.43	0.12	0.30	0.44	0.021	0.034	0.029
Highest month	5.36	83.2	12.28	0.33	5.99	0.44	1.21	0.85	0.36	0.49	0.025	0.044	0.033
1990s	4.66	80.2	13.83	0.29	6.03	0.51	1.21	0.81	0.40	0.50	0.020	0.045	0.039
2000s	1.97	56.6	15.17	0.34	8.13	0.76	0.83	0.34	0.49	0.55	0.019	0.052	0.037
2010s	1.37	47.3	19.55	0.39	11.62	1.03	0.85	0.21	0.64	0.59	0.019	0.053	0.035

Table 2 Mann Kendall trend statistics for selected chemical variables

Determinand	Test Z	Significance	Slope	95% confidence intervals		Unit
				Lower	Upper	
Non-marine SO_4^{2-}	-6.41	***	-0.118	-0.139	-0.098	$\text{mg l}^{-1} \text{yr}^{-1}$
H^+	-5.90	***	-1.08	-1.33	-0.85	$\mu\text{eq l}^{-1} \text{yr}^{-1}$
Al_{total}	-5.72	***	-0.0118	-0.0159	-0.0088	$\text{mg l}^{-1} \text{yr}^{-1}$
Al_{inorg}	-6.39	***	-0.0179	-0.0226	-0.0141	$\text{mg l}^{-1} \text{yr}^{-1}$
Al_{org}	5.92	***	0.0067	0.0049	0.0080	$\text{mg l}^{-1} \text{yr}^{-1}$
Fe	4.86	***	0.0122	0.0089	0.0151	$\text{mg l}^{-1} \text{yr}^{-1}$
DOC	5.78	***	0.1864	0.1508	0.2284	$\text{mg l}^{-1} \text{yr}^{-1}$
Abs ₄₀₀	5.54	***	0.146	0.118	0.177	$\text{m}^{-1} \text{yr}^{-1}$
DON	3.76	***	0.0019	0.0009	0.0029	$\text{mg l}^{-1} \text{yr}^{-1}$
NO_3^-	-0.78		-0.0002	-0.0011	0.0002	$\text{mg l}^{-1} \text{yr}^{-1}$
P_{total}	-0.43		-0.0082	-0.0371	0.0330	$\mu\text{g l}^{-1} \text{yr}^{-1}$
Abs ₄₀₀ /DOC	4.21	***	0.00468	0.00270	0.00609	$\text{l mg}^{-1} \text{m}^{-1} \text{yr}^{-1}$
DON/DOC	-5.76	***	-0.000220	-0.000277	-0.000157	$\text{mg mg}^{-1} \text{yr}^{-1}$
Fe/DOC	2.99	**	0.000389	0.000157	0.000613	$\text{mg mg}^{-1} \text{yr}^{-1}$
$\text{Al}_{\text{org}}/\text{DOC}$	1.04		0.000056	-0.000054	0.000150	$\text{mg mg}^{-1} \text{yr}^{-1}$

Trend significance is denoted as *** = $p < 0.001$, ** = $p < 0.01$ and * = $p < 0.05$

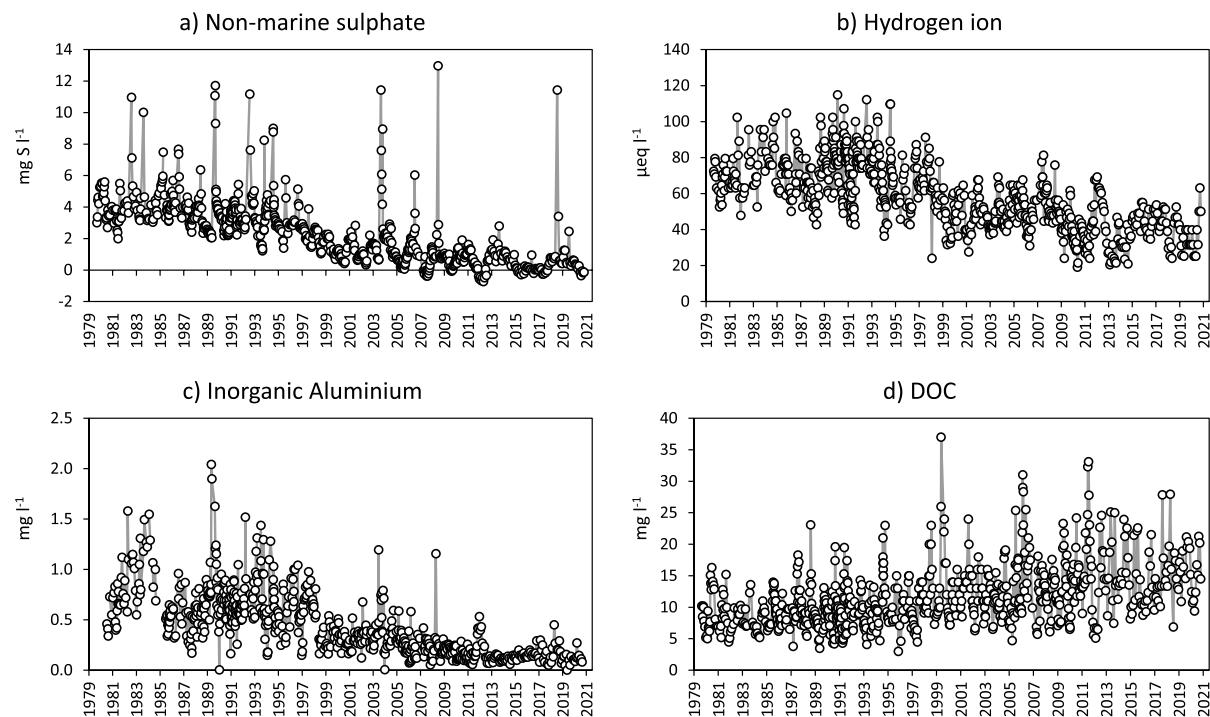


Fig. 1 Concentrations of acidity-related water quality variables (non-marine sulphate, hydrogen ion and inorganic aluminium) and DOC

with the reduction in $x\text{SO}_4^{2-}$, while the decline in Al_{tot} was smaller (35%).

Concentrations of DOC have increased monotonically through the study period, with a 64% increase in decadal mean concentrations from $9.1 (\pm 1.9) \text{ mg l}^{-1}$ in the 1980s to $14.9 (\pm 3.3) \text{ mg l}^{-1}$ in the 2010s. Monthly minimum concentrations showed a smaller (29%) increase, whereas monthly maxima increased by 59%, approximately proportional to the annual mean. Absorbance at 400 nm rose even faster (Fig. 2) with decadal mean values rising by 119% over the study period. Monthly maximum Abs_{400} rose by 94%, and monthly minimum by 68%. In contrast, mean and monthly maximum DON concentrations rose by just 22% and 20% respectively, while monthly minimum concentrations hardly changed. These diverging trends in Abs_{400} and DON are reflected in the ratios normalised by DOC concentration (Fig. 3), with $\text{Abs}_{400}/\text{DOC}$ having increased significantly ($p < 0.001$, Table 2) from a mean of 0.40 in the 1980s to 0.53 in the 2010s, and mean DON/DOC having declined significantly ($p < 0.001$) from 0.026 to 0.020 over the same period. During all time periods, ratios of $\text{Abs}_{400}/\text{DOC}$ were highest in months with the

highest DOC concentrations, and lowest in months with low DOC concentrations, whereas for DON/DOC the opposite pattern was observed (Table 1).

The organic matter associated metals, Fe and Al_{org} , both increased during the monitoring period. Increases were largest for Fe, with decadal mean concentrations increasing by 117%, monthly minimum concentrations by 97% and monthly maximum concentrations by 132%. For Al_{org} , the equivalent values were 85%, 71% and 76%. Consequently, mean ratios of Fe/DOC increased significantly ($p < 0.01$) from 0.035 in the 1980s to 0.045 in the 2010s. Time series data suggest however that Fe/DOC ratios have fluctuated over the monitoring period, with notably low values in the late 1990s followed by an apparent step change up to higher values (Fig. 3c). In contrast to Fe, ratios of $\text{Al}_{\text{org}}/\text{DOC}$ have remained fairly stable, with no significant trend over the full time series.

It is probable that increases in Fe have contributed to increases in Abs_{400} . Kritzberg and Ekström (2012) estimated that absorbance at 420 nm (Abs_{420}) increased by 0.0075 to $0.0090 \text{ m}^{-1} \text{ per mg l}^{-1} \text{ Fe}$. Applying these values to our data suggests that Fe

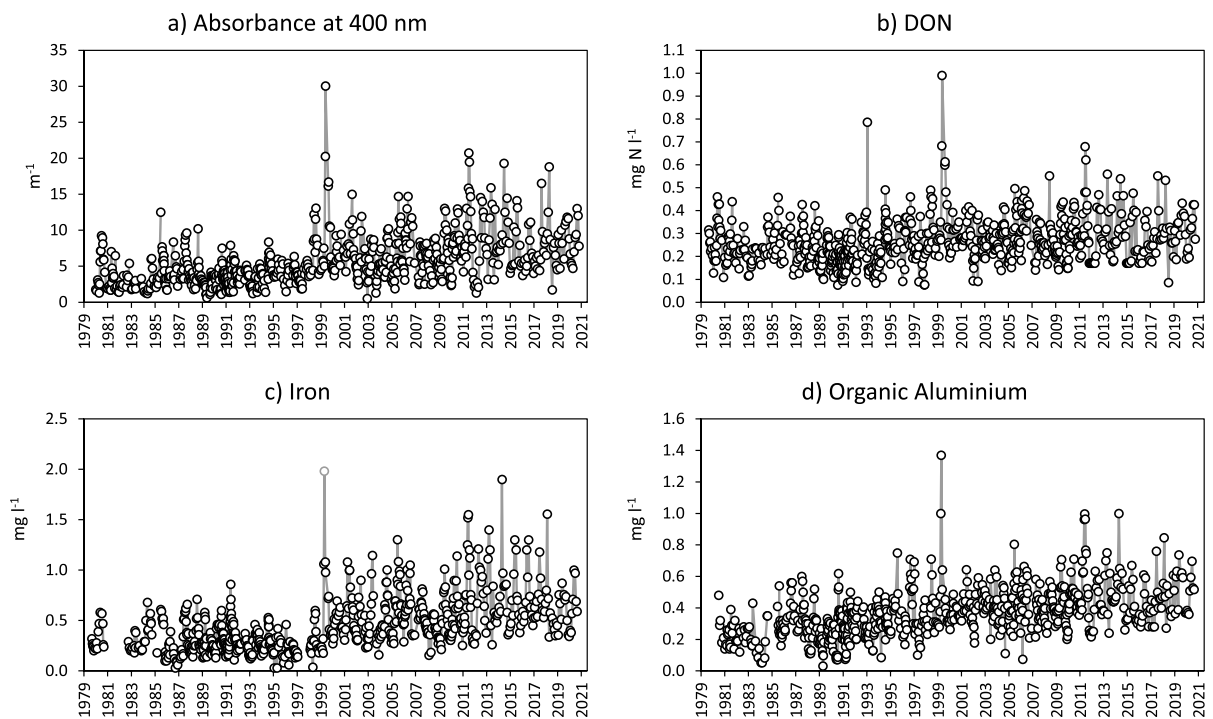


Fig. 2 Concentrations of DOM-related determinands

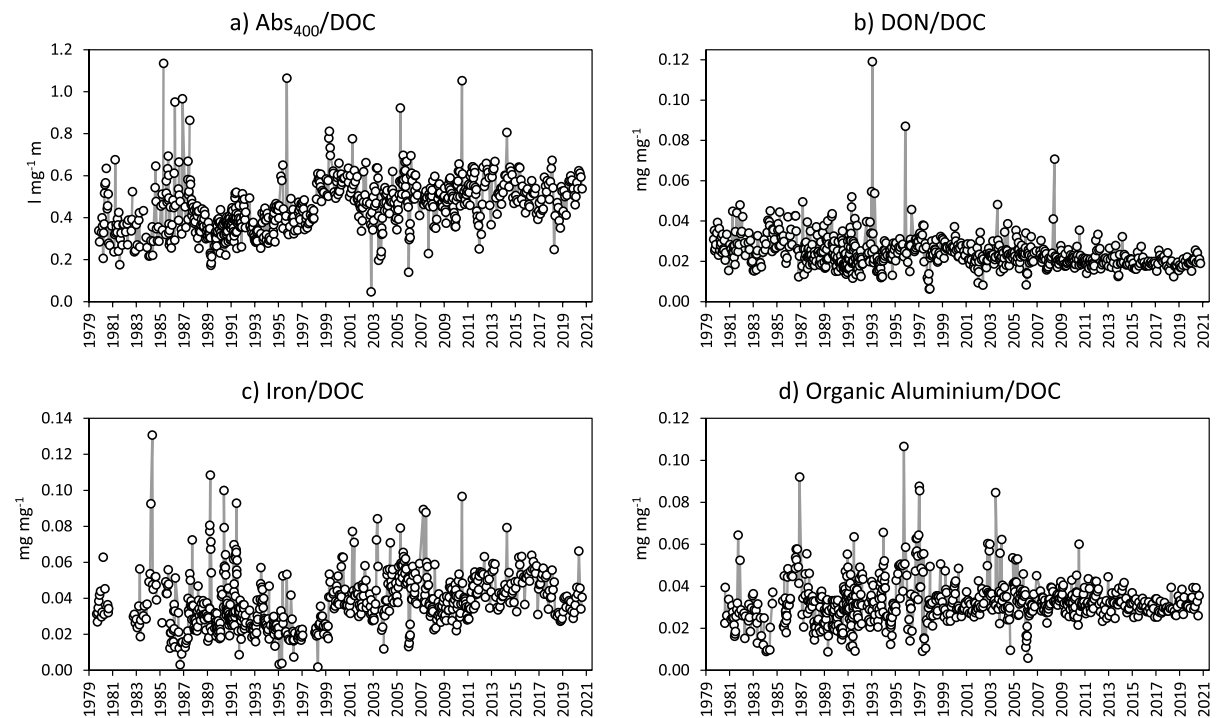


Fig. 3 Ratios of selected determinands to DOC concentration

may have contributed 5–8% of measured absorbance. If we allow for a 50% higher Fe influence on Abs₄₀₀ compared to Abs₄₂₀ (in line with the average ratio of Abs₄₀₀ to Abs₄₂₀ where both are recorded in the Gårdsjön dataset) this contribution rises to 8–11%. The estimated contribution of Fe to total absorbance did not change between time periods. Our analysis suggests that rising Fe could explain 6–11% of the observed increase in Abs₄₀₀ from the 1980s to 2010s.

Discussion

Rising DOC and recovery from acidification

Data from the Gårdsjön F1 stream show that reductions in sulphur emissions and deposition since the 1980s have led to profound changes in streamwater biogeochemistry. The 85% decline in decadal mean xSO_4^{2-} concentrations indicates a return towards pre-industrial background levels. The 78% reduction in mean Al_{inorg} appears directly proportional to the reduction in mean xSO_4 , whilst reductions in H^+ concentration have been markedly

smaller. This can, to a large extent, be explained by the observed offsetting increase in DOC, and thus organic acidity, buffering the reduction in mineral acidity (Evans et al. 2008; Futter et al. 2014). Our results are consistent with those of many previous studies that have inferred a causal link between rising DOC and declining acid deposition (see Introduction). Unlike most previous studies, however, the long duration of the monitoring data from Gårdsjön means that we are able to show that DOC increases have been sustained since the peak of sulphur deposition, which occurred in Sweden in the mid-1980s, through to the present day. While we cannot determine whether DOC concentrations have returned to natural background levels at F1, palaeolimnological studies undertaken at acidification-impacted lakes in Sweden and Canada suggest that DOC has reached pre-acidification levels at some locations, while remaining below natural baselines at others (Bragée et al., 2015; Meyer-Jacob et al. 2015; Valinia et al. 2015; Meyer-Jacob et al. 2020). A few palaeolimnological and monitoring studies even suggest that DOC levels in some lakes may now exceed the pre-industrial baseline, due to climatic changes such as rainfall or temperature

change (de Wit et al. 2021; Monteith et al. 2023) or forest expansion (Meyer-Jacob et al. 2019; Škerlep et al. 2020), although clearly the latter is not universal.

Changes in DOM optical properties

Our results clearly suggest that not only have DOM concentrations risen, but that the visible light absorbance of DOM has risen disproportionately, increasing the specific visible light absorbance (i.e. Abs_{400}/DOC) by an average of 35%. This result is consistent with the limited evidence available from previous studies by Kritzberg and Ekström (2012) and Stetler et al. (2021) who reported increases in Abs_{420}/DOC for large Swedish rivers and Abs_{440}/DOC for lakes in the Adirondack region of the Northeastern United States respectively. Both regions have been historically impacted by acid deposition, and the majority of rivers with increasing trends reported by Kritzberg and Ekström (2012) were in the south of the country, where these impacts were greatest. Our results support those of the previous authors in suggesting that the so-called ‘brownification’ of surface waters across much of Europe and North America is the result not only of increasing DOM export from soils to waters, but also of an increase in the light-absorbing properties of that DOM. Our analysis suggests that 6–11% of the increase in Abs_{400} at Gårdsjön F1 could be due to increases in Fe concentrations. This is lower than the average value of 25% for Sweden reported by Kritzberg and Ekström (2012), but in line with their value of 6% for southern Sweden. However other work suggests that Fe-related absorbance in natural waters may be largely caused by DOM-associated Fe (Xiao et al. 2013), rendering the distinction between DOM- and Fe-related absorbance somewhat meaningless.

Mechanistically, increases in the specific light absorbance of DOM are consistent with increased solubility of more strongly light-absorbing, weakly soluble, high molecular weight ‘hydrophobic’ DOM in response to declining levels of acidity, inorganic Al concentrations and ionic strength in porewaters (e.g. Hruška et al. 2009; Oulehle et al. 2013). This response to declining acidity was demonstrated experimentally in a Swedish plot-scale manipulation study by Ekström et al. (2011). It is broadly consistent

with mechanistic understanding of the processes controlling DOM solubility, and with the limited observations of trends in absorbance/DOC ratios reported previously (Oni et al. 2013; Stetler et al. 2021; Xiao and Riise 2021). Dawson et al. (2009) reported decreases in specific ultraviolet absorbance at 250 nm ($SUVA_{250}$) at two Scottish upland catchments, but measurements in the earlier part of the record (many values $> 8 \text{ l mg}^{-1} \text{ m}^{-1}$) appear to be outside the range of observations for other natural waters (e.g. Anderson et al. 2019), suggesting a possible methodological explanation.

Changes in DOM stoichiometry

While DON concentrations did increase slightly at Gårdsjön, these increases were far smaller than those in DOC, and consequently the ratio of DON/DOC decreased substantially (Fig. 3b, Table 1). Expressed as the more commonly reported inverse ratio, DOC/DON rose from 38.8 in the 1980s to 51.3 in the 2010s. With inorganic N concentrations consistently low throughout the study period ($< 0.2 \text{ mg N l}^{-1}$), DON comprises the majority of the aquatic N pool, and these ratios suggest acute and intensifying N-limitation of heterotrophic activity, and potentially of the wider food web. Furthermore, it is likely that a large fraction of the N contained in terrestrially-derived DOM is not readily bioavailable (e.g. Berggren and del Giorgio, 2015; Stutter et al. 2018; Graeber et al. 2021), and this fraction is likely to have increased as the ratio of DON to DOC has declined. According to our mechanistic interpretation above, the observed trend in DON/DOC is consistent with increasing mobilisation of hydrophobic, biologically recalcitrant DOM from the soil as the suppressive effect of high acidity and ionic strength on organic matter solubility has decreased over the last 40 years. Although NO_3^- concentrations at Gårdsjön F1 were low, data from a wider regional study in southwest Sweden (Peacock et al. 2022) and from other historically acidification-impacted regions (e.g. Ryan and Lawrence 2024) indicate that NO_3^- concentrations have decreased as DOC concentrations have increased. Taken together with our evidence of declining DON/DOC ratios, this points towards intensifying N-limitation of headwater ecosystems.

Dissolved organic phosphorus (DOP) concentrations are rarely measured, and were not available for the Gårdsjön study, but may be an important component of the aquatic nutrient supply in some water bodies (Bentzen et al. 1992; Thompson and Cottner, 2018; Yates et al. 2019). In general, however, we would expect the P content of DOM to be highest in more bioavailable, low molecular weight compounds (Thomson and Cottner, 2018), rather than the more biologically recalcitrant, high molecular weight compounds which our Abs_{440}/DOC and DON/DOC data suggest have increased by the largest proportion at Gårdsjön. Furthermore, P_{tot} concentrations have remained continuously low (annual means $< 10 \mu\text{g l}^{-1}$) with no trend over the monitoring period (Table 2). It therefore seems likely that, as for N, long-term increases in DOM export have intensified P-limitation of biological activity in the Gårdsjön F1 stream, and in downstream ecosystems. A regional assessment of stoichiometric changes in surface waters in the region surrounding the Gårdsjön study area (Peacock et al. 2022) supports this interpretation. Our results are also consistent with previous regional studies of long-term changes in the stoichiometry of Swedish headwaters and lakes by Isles et al. (2018) and Huser et al. (2018), both of which found evidence of widening DOC/P_{tot} ratios, although in the Huser et al. study there was evidence of declining P_{tot} concentrations (as well as rising DOC) whereas in the Isles et al. study (as at Gårdsjön F1) concentrations of P_{tot} were generally stable. Isles et al. (2018) also reported a decline in the ratio of inorganic N to P_{tot} , suggesting intensifying N limitation of aquatic primary production, but this was not apparent at Gårdsjön F1 where inorganic N and P_{tot} were both continuously low.

Changes in organic matter associated metals

Both Fe and Al_{org} have increased in line with the increase in DOC, whereas Al_{inorg} has declined in proportion to the reduction in xSO_4^{2-} concentrations. The proportional increase in average Fe (117% from the 1980s to 2010s) was larger than the equivalent increase in DOC (64%) and more similar to the increase in Abs_{400} (119%). This suggests that higher Fe export from the soil may be primarily associated with the increasing export of humic, highly coloured DOM as discussed above. Knorr (2013) previously

noted highly synchronous behaviour of DOC and Fe on timescales ranging from episodic to decadal in a German forest stream, but postulated that DOC may be responding to changes in the Fe cycle, rather than the reverse. As discussed earlier, several other studies have reported a close correspondence between long-term Fe and DOC trends, although some have discounted a direct causal relationship (Kritzberg and Ekström, 2012) or argued that both trends are partly or wholly attributable to factors other than declining S deposition and recovery from acidification, such as forest expansion or changes in rainfall (Björnerås et al. 2017, 2022; Kritzberg et al. 2020). At our study site, the only land-cover change has been aging of the forest stand, which was already over 100 years old at the start of monitoring. Elsewhere, concurrent Fe and DOC trends have been observed in catchments described as pristine forest (Xiao and Riise 2021) and in catchments with no tree cover (Neal et al. 2008). The results of our study suggest a direct mechanistic link between recovery from acidification and rising Fe, as previously suggested by Neal et al. (2008) and Xiao and Riise (2021). This could occur via the increased mobility of Fe in organically complexed forms (Neal et al. 2008; Oni et al., 2013; Škerlep et al. 2023), or via effects of declining SO_4 concentrations on redox processes. The latter mechanism could involve reduced Fe and S co-precipitation in sulphides such as pyrite (Bottrell et al. 2007; Johnston et al. 2014), or reduced competition for organic substrates by sulphate reducing bacteria, favouring reduction of insoluble Fe(III) to soluble Fe(II) (Chappelle and Lovley, 1992). We cannot exclude the possibility that increased soil wetness due to rising rainfall over the monitoring period could also have played a role in rising Fe concentrations, as suggested by Kritzberg and Ekström (2012) and others, and the extent of apparently cyclical variability in the Fe/DOC ratio at F1 (Fig. 3c) also suggests that climatic variability such as wet-dry cycles may influence Fe leaching relative to that of DOC via effects on redox cycles. However it is also noteworthy that the upward shift in Fe concentrations around 1998 coincided with a sharp fall in Al_{inorg} (compare Figs. 1c and 2c), which could indicate a reduction in competition between Al and Fe for available complexing sites on the DOM (Perdue et al. 1976). Overall, we consider it likely that reductions in acid deposition have been the

dominant driver of rising Fe concentrations at the F1 catchment, and more widely.

Compared to Fe, the proportional increase in Al_{org} over the same period of 85% is more similar to the increase in bulk DOC. This could indicate that Al does not bind preferentially with the more coloured, weakly soluble DOM mobilised following reductions in acid deposition, or alternatively that the competitive effect proposed above affects the capacity of Fe to form organic complexes to a greater extent than Al. It is also possible that the observed increase in Al_{org} represents the net effect of two competing changes, namely the decrease in overall Al mobilisation from the soil due to decreasing acidity (as evidenced by the reduction in Al_{tot}) versus the increased proportion of mobilised Al that is organically complexed due to rising DOM concentrations. In general, our results are consistent with previous studies showing a reduction in surface water Al_{inorg} and an increase in Al_{org} in other regions undergoing recovery from acidification (e.g. Strock et al. 2014; Lawrence et al. 2021).

Ecological implications of observed changes

There is a growing body of evidence to suggest that rising DOC concentrations have affected multiple aspects of aquatic ecosystem functioning, both directly via changes in the chemical environment, and indirectly via changes in light penetration and subsequently the photic depth, thermal regime and stratification of lakes (e.g. von Einem and Granéli 2010; Williamson et al. 2015; Leach et al. 2019; Kritzberg et al. 2020; Frigstad et al. 2023). Potential chemical impacts include changes in the availability of nutrients and the toxicity of metals, as well as changes in substrate availability for heterotrophic bacteria (Jansson et al. 2000; Porcal et al. 2009). Changes in light regime have the potential to reduce rates of benthic and pelagic primary production, affecting food supply for zooplankton, while reduced visibility could affect predator success, for example by reducing fish production (Ranåker et al. 2012; Jönsson et al. 2013; Feuchtmayr et al. 2019). On the other hand, absorption of UV-B radiation by DOM can provide some protection against damage to the photosynthetic systems of various algal groups, including to the electron transport chain of photosystem II (PS II) (Häder et al. 2011), and DNA in both prokaryotic and eukaryotic components

of algal biofilms (Singh et al. 2010). Given that ecological responses linked to changing light penetration depend on the light-absorbing properties of the DOM, our results showing an increase in the ratio of Abs_{400} to DOC indicate that these impacts could be more acute than monitoring of bulk DOC concentration alone would suggest. Solomon et al. (2015) suggested that higher light absorption and higher nutrient concentrations with rising DOM concentrations could have opposing effects on aquatic primary production. Our data, showing declining DON/DOC ratios at Gårdsjön, suggest that both light and nutrient limitation of the aquatic ecosystem could be intensifying.

Overall, these changes are likely to further exacerbate the established tendency for 'brownification' to drive lakes from autotrophic to heterotrophic dominance (e.g. von Einem and Granéli 2010). While such changes to the colour of water and availability of DOM may be perceived as ecologically or societally negative, for example if they lead to reductions in aquatic macrophyte depth or fish populations, our results support the view that these changes form an element of ecological recovery (along with increasing pH and decreasing inorganic Al) from past anthropogenic perturbation by acid deposition, rather than ecological degradation.

The observed increases in Fe concentrations could have influenced both light levels and wider ecosystem functioning in the F1 catchment and in downstream receiving waters. Surface waters with very high Fe concentrations, such as those draining acid sulphate soils, may be ecologically impoverished due to minimal light penetration and deposition of Fe hydroxides onto vegetation (e.g. Vuori 1995). Kritzberg and Ekström (2012) investigated the potential contribution of increasing Fe concentrations to increasing visible light absorbance, and based on experimental Fe additions found that Abs_{420} increased by an average of 0.83 m^{-1} per mg l^{-1} of Fe added. Based on the observed Fe increase at F1 from the 1980s to the 2010s of 0.36 mg l^{-1} , and applying a conversion factor of $Abs_{420} = 0.729 Abs_{400}$ (based on concurrent measurements on a subset of samples), we estimate that this may have increased Abs_{400} by 0.41 m^{-1} , i.e. around 7% of the observed total increase. Kritzberg and Ekström (2012) found spatial variation in the contribution of Fe to water colour across Sweden, with about 6% of the variation

explained by Fe in the south (consistent with our results) and 74% in the north. Increased export of Fe may also affect downstream aquatic ecosystems; Fe is a limiting nutrient in some marine ecosystems, and it has been suggested that DOM binding of riverine Fe could increase the proportion of Fe exported through estuaries. However, previous work at Lake Mälaren in Sweden found that Fe was efficiently removed within the lake, with a half-life of 0.6 year compared to 1.7 years for Abs_{420} and 6.1 years for DOC (Köhler et al. 2013), and Weyhenmeyer et al. (2014) showed a negative relationship between Fe concentration and water retention time at a broad landscape scale. In the specific case of the F1 catchment, the stream flows directly into Lake Gårdsjön below the sampling point, which has a mean water residence time of 1.1 years (Johannsen and Nilsson, 1985), suggesting that the majority of Fe from this stream may be removed within the lake by a combination of photo-degradation and flocculation processes. In-lake DOM losses are enhanced by photo-degradation in the presence of Fe due to the photo-Fenton reaction (Vähätalo 2009). Likewise, the removal by DOM by flocculation is enhanced in the presence of Fe (Lalonde et al. 2012). More generally, however, evidence of Fe increases in some lakes and larger rivers (e.g. Neal et al. 2008; Kritzberg and Ekström, 2012; Björnerås et al. 2017) suggests that a proportion of the Fe exported from other headwater streams is likely to be impacting on downstream ecosystems, potentially extending to coastal marine areas.

The marked reduction in Al_{inorg} observed in headwater streams such as F1 will undoubtedly have had a positive impact on aquatic ecosystems, reversing the historic impacts of acidification on fish, aquatic invertebrates and other biota. Because Al_{org} has lower toxicity than Al_{inorg} , the increase in Al_{org} is not expected to have had a major counteracting effect, and indeed the higher proportion of remaining Al now in organic form may have amplified the overall benefits of reduced acid deposition.

Conclusions

Gårdsjön F1 is one of very few long-term catchment studies in which both DOM quantity and quality have been systematically monitored since the peak of acid deposition. We recognise the need

for caution in interpreting data from a single monitoring site. However the strong consistency between observed trends in sulphur, Al, pH and DOC at Gårdsjön with those observed across Sweden (Futter et al. 2014) and elsewhere in Northern Europe (e.g. Monteith et al. 2014; Lepistö et al. 2021), together with the generally high spatiotemporal coherence of headwater catchment water quality trends (e.g. Watmough et al. 2004; Evans et al. 2010; Futter et al. 2014), suggest our observations from this site may be indicative of those that have occurred across larger spatial scales. As the F1 catchment is primarily a forested site with low percent wetland, this supports previous findings that solubility-driven processes are not constrained to peatlands, but can also occur in the organic horizons of organo-mineral soils (Evans et al. 2012).

Our findings that absorbance has risen faster than DOC, whereas DON has risen more slowly, are consistent with our hypotheses that there has been a solubility-driven shift in the molecular composition of surface water DOM towards a higher proportion of coloured, aromatic, nitrogen-poor, but potentially poorly decomposed organic compounds. This shift has clear implications for the light, energy and nutrient regimes of aquatic ecosystems, for example by disadvantaging visual predators, altering the availability of DOM for heterotrophic microbial metabolism, and intensifying N (and potentially also P and light) limitation. Accompanying (and apparently causally linked) increases in Fe and Al_{org} may also affect aquatic ecosystem functioning. Given that all of these changes appear to be a response to decreasing acid deposition, we caution against interpreting them as evidence of ecological degradation, or as problems that require mitigation through changes in land-management. While there are likely to be ‘winners’ and ‘losers’ within aquatic food webs, it appears that previously perturbed ecosystems are returning to a more heterotrophic, organic matter- and iron-rich, nutrient-poor, and darker natural state.

Author contributions All authors contributed to the development of the study, including conceptualisation, funding acquisition and project implementation. Data collection at Gårdsjön was led by Filip Moldan and Sarah Jutterström. The first draft of the manuscript was written by Chris Evans with support for data analysis by Mike Peacock and Martyn Futter and contributions to interpretation and writing by all

authors. All authors read and approved the final version of the manuscript.

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Data availability Data used in the study are available via the MVM-database at SLU: <https://miljodata.slu.se/MVM/>, or directly from the co-authors Filip Moldan and Sara Jutterström on request.

Declarations

Competing interests The authors declare no relevant financial or non-financial interests.

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