

# Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate

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## Abstract

Increasing concentrations of organic matter (OM) in surface waters have been noted over large parts of the boreal/nemoral zone in Europe and North America. This has raised questions about the causes and the likelihood of further increases. A number of drivers have been proposed, including temperature, hydrology, as well as  $\text{SO}_4^{2-}$ - and  $\text{Cl}^-$  deposition. The data reported so far, however, have been insufficient to define the relative importance of different drivers in landscapes where they interact. Thirty-five years of monthly measurements of absorbance and chemical oxygen demand (COD), two common proxies for OM, from 28 large Scandinavian catchments provide an unprecedented opportunity to resolve the importance of hypothesized drivers. For 21 of the catchments, there are 18 years of total organic carbon (TOC) measurements as well. Despite the heterogeneity of the catchments with regards to climate, size and land use, there is a high degree of synchronicity in OM across the entire region. Rivers go from widespread trends of decreasing OM to increasing trends and back again three times in the 35-year record. This synchronicity in decadal scale oscillations and long-term trends suggest a common set of dominant OM drivers in these landscapes. Here, we use regression models to test the importance of different potential drivers. We show that flow and  $\text{SO}_4^{2-}$  together can predict most of the interannual variability in OM proxies, up to 88% for absorbance, up to 78% for COD. Two other candidate drivers, air temperature and  $\text{Cl}^-$ , add little explanatory value. Declines in anthropogenic  $\text{SO}_4^{2-}$  since the mid-1970s are thus related to the observed OM increases in Scandinavia, but, in contrast to many recent studies, flow emerges as an even more important driver of OM variability. Stabilizing  $\text{SO}_4^{2-}$  levels also mean that hydrology is likely to be the major driver of future variability and trends in OM.

*Keywords:* climate, DOC, hydrology, recovery from acidification, sulphate, time series, water quality

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## Introduction

Organic matter (OM) is a key component of water chemistry. Increasing concentrations of OM in surface waters have been noted over large parts of the boreal/nemoral zone in Europe and North America (Monteith *et al.*, 2007). If widespread increases in OM concentrations continue, they will have profound implications for

drinking water and aquatic ecosystems. Several explanations related to a warmer climate have been proposed for the OM increases (Schindler, 1998; Eikebrokk *et al.*, 2004; Weyhenmeyer *et al.*, 2004). Temperature increases and their influence on microbial processes were proposed as the explanation of increases in 22 lakes and streams from small (most  $<10 \text{ km}^2$ ), acid-sensitive catchments in the United Kingdom (Freeman *et al.*, 2001). Increased runoff has been cited as the cause of increased colour in Sweden during the 1980s (Forsberg, 1992), and more recently in Norway (Hongve *et al.*,

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2004). Worrall & Burt (2007) also found hydrology to be the major controlling factor for dissolved organic carbon (DOC) flux in rivers in Great Britain. Other authors, however, have used data from process studies (Clark *et al.*, 2005) and other sites to arrive at a revised explanation that OM patterns have been driven largely by decreases in  $\text{SO}_4^{2-}$  and variation in marine  $\text{Cl}^-$  deposition (Evans *et al.*, 2006; Vuorenmaa *et al.*, 2006). High concentrations of these anions reduce the solubility of OM by decreasing pH and increasing ionic strength (Kalbitz *et al.*, 2000). Stimulation of primary production by increased nitrogen deposition (Pregitzer *et al.*, 2004) and  $\text{CO}_2$  levels (Freeman *et al.*, 2004) have also been discussed as potential influences on OM.

The recent support for declining  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  deposition as the primary driver of OM increases was met by a cautionary note (Roulet & Moore, 2006) about the difficulty of resolving the importance of potential drivers in landscapes where processes interact at different spatial and temporal scales.

The difficulty of resolving these interactions is compounded by the dearth of analyses on regional data sets extending back more than two decades to a time when  $\text{SO}_4^{2-}$  deposition was still increasing. This study presents monthly OM data in the form of absorbance and chemical oxygen demand (COD) measurements from 28 large (210–26 800 km<sup>2</sup>) rivers in Sweden sampled during 1970–2004. The same methodology has been used for absorbance and COD analysis in the same laboratory during the entire period. For 21 of the rivers, there are also 18-year records of total organic carbon (TOC) concentrations, 1987–2004. By trying to predict annual mean values of the different OM measures from linear regression, we investigate the importance of four potential variables as candidate drivers of the patterns in annual OM variability. These candidate drivers are antecedent flow and air temperature, as well as the  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  concentrations measured in the same monthly water sample as the OM measures.

## Materials and methods

The 28 catchments represent the diversity that can be found in a 1000 km, N-S swath of the boreal/nemoral zone, with respect to land use, water chemistry, temperature and runoff. They are relatively large (>200 km<sup>2</sup>), with dominant catchment land covers including agricultural, forest and alpine areas (Table 1).

The rivers are included in national or regional monitoring programs with monthly sampling. Three different measures of OM have been used. The absorbance has been measured 1970–2004 on filtered (filter size 0.45 µm) samples. It is measured as absorbance at 420 nm wavelength in a 5 cm cuvette. COD has been

**Table 1** Catchment and water chemistry characteristics

Parameter	Range	Median
Latitude	57°11'–65°35'	59°35'
Longitude	12°30'–19°17'	14°06'
Catchment size (km <sup>2</sup> )	210–26 800	2300
Wetland (%)	0.6–16	5
Agriculture (%)	0–48	7
Forest (%)	36–85	65
Alpine (%)	0–46	0
Mean runoff (mm yr <sup>-1</sup> )	170–860	380
Mean air temperature (°C)	–0.2 to 7.0	5.9
Mean absorbance (at 420 nm) (m <sup>-1</sup> )	0.4–4.6	2.0
Mean COD (mg [O] L <sup>-1</sup> )	2.5–22.8	8.0
Mean TOC (mg L <sup>-1</sup> ) (1987–2004)	2.4–17.1	7.8
Mean pH	6.6–7.7	7.0
Mean $\text{SO}_4^{2-}$ (meq L <sup>-1</sup> )	0.044–1.73	0.17
Mean $\text{Cl}^-$ (meq L <sup>-1</sup> )	0.026–1.02	0.14
Mean total Fe (µmol L <sup>-1</sup> )	0.68–18	5.4

COD, chemical oxygen demand; TOC, total organic carbon.

measured on unfiltered samples as consumption of  $\text{KMnO}_4$  according to national standards (SLU, 2007) 1970–2004. The consumption of  $\text{KMnO}_4$  is converted to COD(Mn) (mg [O] L<sup>-1</sup>) according to  $\text{COD(Mn)} = \text{KMnO}_4/3.95$  (mg L<sup>-1</sup>). COD(Mn) usually comprises ca. 40% most easily degradable fraction of the total organic material (Wilander, 1988). For 21 of the rivers, TOC concentrations have also been measured 1987–2004 by oxidative combustion on unfiltered samples. The calculations done for this period are always based on the smaller subset of 21 rivers, including the calculations regarding absorbance and COD. Earlier studies in Fenno-Scandia's boreal forest areas have shown that total and DOC (defined as that organic carbon that can pass a 0.45 µm filter) differ by <10%, and usually <5%, under a variety of flow conditions (Ivarsson & Jansson, 1994; Gadmar *et al.*, 2002; Mattsson *et al.*, 2005). Therefore, we consider our results for unfiltered OM (COD, TOC) to be essentially equivalent to that of the filtered fraction (absorbance).

For the whole subset of data with TOC measurements, COD correlates to TOC with an  $r^2$  of 0.81 (4502 paired observations). With the removal of 25 outliers, the  $r^2$  increases to 0.88, with the relationship  $\text{TOC (mg L}^{-1}\text{)} = 0.51 + 0.84 \times \text{COD (mg [O] L}^{-1}\text{)}$ . The COD(Mn) measured in oxygen equivalents has approximately the same numerical value as TOC measured in mg L<sup>-1</sup>. The correlation between absorbance and TOC is lower, with an  $r^2$  of 0.64 for the whole data set. With the removal of 25 outliers (same as above),  $r^2$  increases to 0.67, where  $\text{TOC (mg L}^{-1}\text{)} = 3.4 + 2.1 \times \text{absorbance (m}^{-1}\text{)}$ . The mean ratio absorbance/TOC is more variable than the ratio

COD/TOC among the catchments; the mean ratio for absorbance/TOC is in the range 0.15–0.37, whereas the mean ratio COD/TOC is between 0.94 and 1.28. One possible reason is that the absorbance is affected by other factors than OM concentrations alone; in particular different Fe complexes contribute to light absorbance and colour in freshwater. The total Fe concentrations have been measured since the early 1970s for 15 of the studied rivers, and since the early 1980s for another three of them. The measurements of Fe ended in 1998 for five of the rivers.

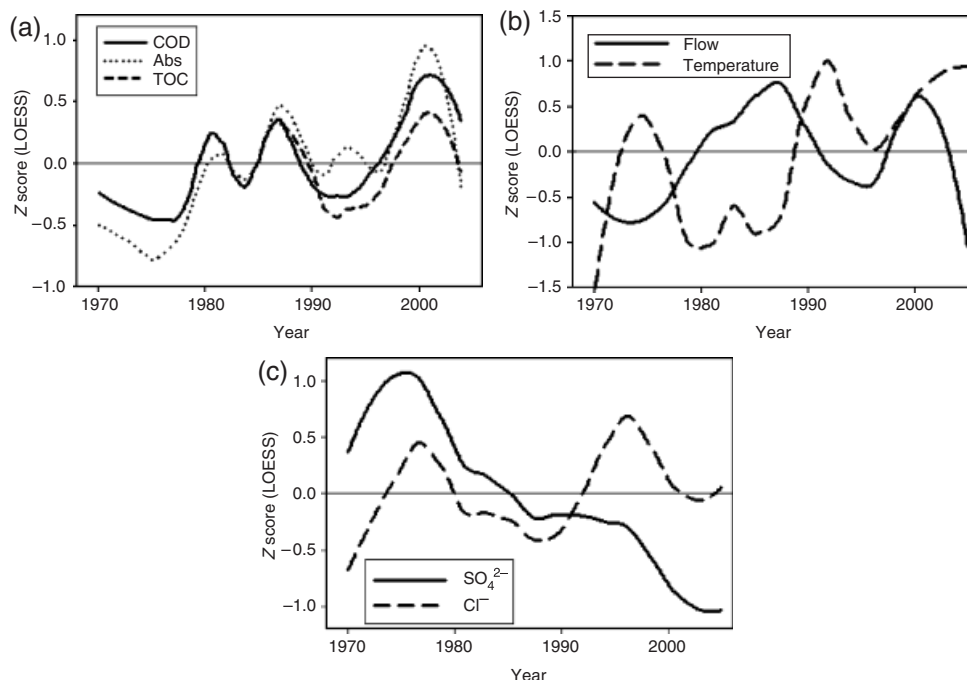
$[\text{SO}_4^{2-}]$  and  $[\text{Cl}^-]$  were measured using ion chromatography according to national standards (SLU, 2007). For the period 1970–1983,  $[\text{SO}_4^{2-}]$  was measured with the Mackereth method (Mackereth, 1955), which has been corrected using data with parallel analysis of the two  $\text{SO}_4^{2-}$  methods.

Records of monthly mean air temperature were taken from meteorological stations, at a maximum distance of 100 km from the watercourse. Monthly flow data were observed or modelled by the Swedish Meteorological and Hydrological Institute (SMHI). Flow was measured daily during the whole period for 19 of the rivers. On the other nine rivers, flow was modelled on a weekly or monthly interval for the periods when daily observations were not available.

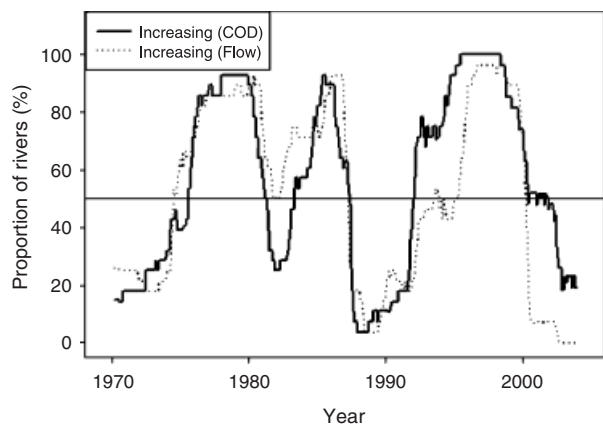
To examine the importance of different drivers and combinations of drivers, linear regression models were

constructed with annual means of OM measures as the response variable. Flow, temperature and annual means of  $[\text{SO}_4^{2-}]$  and  $[\text{Cl}^-]$  were the explanatory variables. Running averages of antecedent flow and air temperature were used, with the period length individually optimized for each watercourse and for each measure of OM. For each sampling occasion, mean antecedent values were calculated over periods of 1, 2, 3, 6, 12 and 24 months for flow and 1, 3, 6, 12, 24 and 36 months for temperature, as suggested by Evans *et al.* (2005). The lengths of time over which the means had been integrated that gave the highest  $r^2$ -value were used in further analysis. Regression models were constructed with all four explanatory variables separately, and then with two or more variables in multiple linear regression (MLR) models. Because concentrations of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  are strongly affected by hydrological conditions, and because we want to assess the effects of long-term, atmospheric deposition-related changes in these anions, an alternative is to examine the correlations between OM and the flow-normalized concentrations (Stålnacke & Grimvall, 2001). In addition, correlations between the ratios of absorbance/TOC, COD/TOC, absorbance/COD and the respective drivers were examined, as well as correlations between Fe concentrations and flow.

To generate smoothed trends in OM concentrations and the explanatory variables for illustrative purposes (Figs 1 and 2), LOESS smoothing (Cleveland & Devlin,



**Fig. 1** Trends in organic matter (OM) (a), flow and temperature (b),  $[\text{SO}_4^{2-}]$  and  $[\text{Cl}^-]$  (c), 1970–2004. The curves describe the median Z score (normalized value) of the time series from the 28 studied rivers smoothed with LOESS.

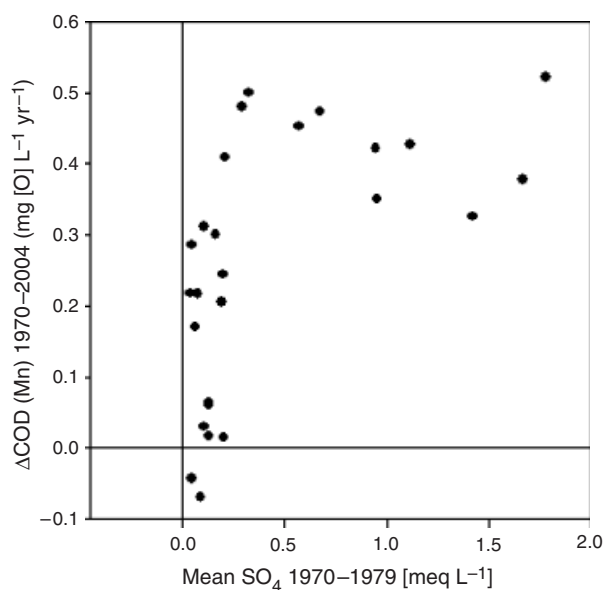


**Fig. 2** Illustration of the synchrony of trends in chemical oxygen demand (COD) and flow among the studied rivers. Percentage of the 28 rivers with an increasing trend in COD (solid) and flow (dotted) during 1970–2003, as defined by the LOESS curve fitted to each time series.

1988) was applied with a span of 0.375; for the shorter time period 1987–2004, a span of 0.75 was used. The span indicates the proportion of observations used by the technique in each local regression. The size of the span determines the resolution of the trends. The LOESS smoothing is equivalent to a running mean value, but with the short-term variations evened out. For time series of 35 years length, a span of 0.375 gives approximately the same result as a running 5-year mean value. To detect any long-term, linear trends over the period, Theil's slope (Helsel & Hirsch, 1992) was used, a nonparametric method where the slope is approximated as the median value of all the pairwise slopes in the time series.

## Results

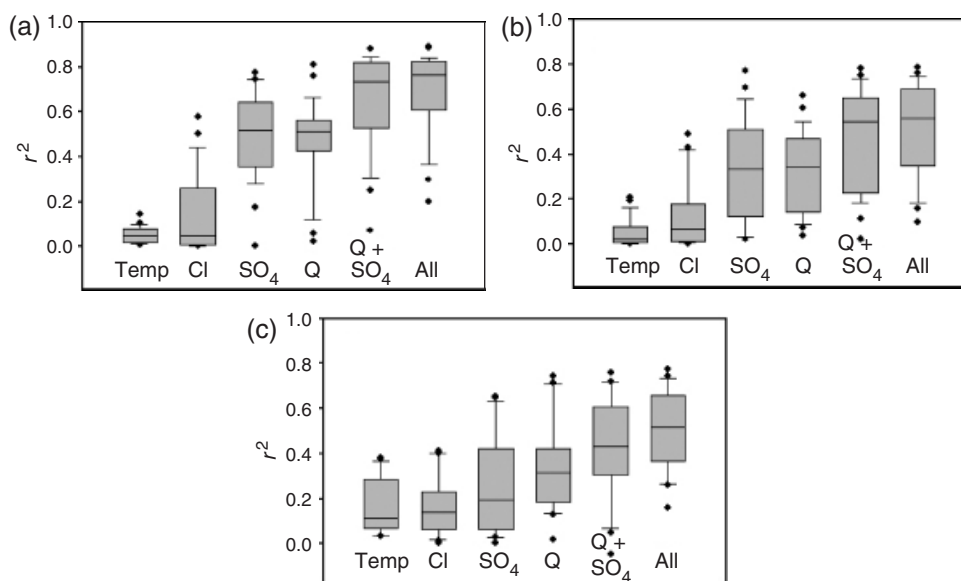
With a data record of 35 years length, it is possible to examine both the general trend, as well as shorter term variability. The overall pattern for the three different measures of OM is the same, with several periodic reversals in the direction of the trends occurring simultaneously for all measures (Fig. 1). In addition there is a linear component of increasing OM during the entire period. What differs between the different OM measures is the magnitude of that trend. The increase in absorbance is most pronounced, with a median annual increase of 1.47% between 1970 and 2004, and 1.14% between 1987 and 2004. The increase in COD is also considerable. The median annual COD increase between 1970 and 2004 is 0.76%, and 0.71% between 1987 and 2004. In contrast, the increase in TOC is smaller and negligible for some rivers. The median annual increase in TOC is 0.27% since 1987.



**Fig. 3** Increase in organic matter (OM) plotted against sulphate concentrations. The change in COD(Mn) ( $\text{mg [O] L}^{-1} \text{ yr}^{-1}$ ) during 1970–2004 for 26 of the rivers, plotted against mean sulphate concentrations during 1970–1979. Two rivers were removed from the plot, these have high concentrations of both  $\text{SO}_4^{2-}$  and OM, and are likely affected by point sources.

The most striking pattern is the degree of synchrony in OM trends for the studied rivers. Increases and decreases in OM concentrations occur simultaneously for all the studied rivers, and these are strongly correlated to periods of increasing or decreasing flow (Fig. 2). If the trend is defined by the LOESS curves, there were periods of increasing absorbance and COD around 1978 and 1985 in over 90% of the studied rivers, as well as an extended period of increasing absorbance and COD in all rivers, 1995–1998. This coincides with increasing flow in almost all rivers. Consequently, there are periods with declining OM concentrations in a large majority of the rivers, centred around 1970, 1988 and 2004, coinciding with periods of decreasing flow.

The OM increase is strongly dependent on the initial  $[\text{SO}_4^{2-}]$ . Rivers with low  $[\text{SO}_4^{2-}]$  levels (16 rivers, mean  $[\text{SO}_4^{2-}]$  1970–1979  $< 0.25 \text{ meq L}^{-1}$ ) all show no increase or intermediate increase during 1970–2004 in COD and absorbance. The 10 rivers with higher  $[\text{SO}_4^{2-}]$  levels all have more pronounced increases in COD and absorbance, in COD between 0.33 and 0.52 ( $\text{mg [O] L}^{-1} \text{ yr}^{-1}$ ) (Fig. 3), and in absorbance between 0.042 and 0.092 ( $\text{m}^{-1} \text{ yr}^{-1}$ ). Two rivers are exceptions to this pattern (data not shown). One of them has steadily increasing  $[\text{SO}_4^{2-}]$  despite the declining atmospheric deposition. The other is situated in an urban area, and has very high  $[\text{SO}_4^{2-}]$  ( $\sim 2.5 \text{ meq L}^{-1}$ ), whereas the OM level remains constant



**Fig. 4** The variance in organic matter (OM) explained by the different potential drivers. Box plot (10th, 25th, 50th, 75th and 90th percentiles marked) of the  $r^2$ -values for annual mean absorbance (a), chemical oxygen demand (COD) (b) and total organic carbon (TOC) (c), modelled with linear regression for 28 rivers, using temperature,  $[\text{Cl}^-]$ ,  $[\text{SO}_4^{2-}]$  and flow as explanatory variables. Combinations of these parameters were modelled using multiple linear regression (MLR). For these models, adjusted  $r^2$ -values are displayed.

during the period. The behaviour of these rivers suggests that they have point sources of  $\text{SO}_4^{2-}$  that make them inappropriate for inclusion in this study.

The importance of flow and  $[\text{SO}_4^{2-}]$  as drivers of OM concentrations is also manifested in the regression modelling (Fig. 4). These are the individual variables that explained the greatest variation for all measures of OM in the majority of the rivers. For absorbance, the median  $r^2$  when using flow alone was 0.51, for COD it was 0.34 and for TOC it was 0.31.  $[\text{SO}_4^{2-}]$  as the sole predictor yielded a median  $r^2$  of 0.52 for absorbance, 0.33 for COD and 0.19 for TOC. If flow-normalized concentrations of  $\text{SO}_4^{2-}$  are used instead of the actual concentrations, the median  $r^2$ -values decrease to 0.48 for absorbance, to 0.27 for COD and to 0.15 for TOC.  $[\text{Cl}^-]$  contributed little to prediction of OM variability; the median  $r^2$  was 0.05 for the absorbance, 0.06 for COD and 0.13 for TOC. Flow normalization of  $[\text{Cl}^-]$  did not change the  $r^2$ -values, except for TOC for which it decreased to 0.10. For a few of the rivers,  $[\text{Cl}^-]$  is an important predictor, with  $r^2$  up to 0.40 for TOC, up to 0.45 for COD and up to 0.57 for absorbance. These are predominantly rivers located in the southwest of Sweden, where there are considerable sea salt contributions to atmospheric deposition. Temperature contributed a low degree of explanation for almost all the studied rivers; the median  $r^2$  was 0.05 for absorbance, 0.02 for COD and 0.11 for TOC. Furthermore, for COD and TOC, the temperature is more often negatively than positively

correlated with OM concentrations, in contrast to what has been hypothesized (Freeman *et al.*, 2001).

When combining different variables to model COD with MLR, flow and  $[\text{SO}_4^{2-}]$  together explain significantly more of the variance in COD than either parameter alone, with a median-adjusted  $r^2$  of 0.73 for absorbance, 0.54 for COD and 0.41 for TOC (Fig. 4). When adding  $[\text{Cl}^-]$  and temperature to the model, the median-adjusted  $r^2$  for absorbance was 0.76 for absorbance, 0.56 for COD and 0.52 for TOC. Thus,  $[\text{Cl}^-]$  and temperature only contribute marginally to the degree of explanation, except for TOC.

The absorbance/TOC ratio has increased in 19 of 21 rivers, significant at 95% level for nine of them. The median ratio was 0.272 [ $\text{m}^{-1}/(\text{mg L}^{-1})$ ] in 1987 and 0.31 in 2004. The COD/TOC ratio has increased in all 21 rivers, significant at the 95% level for 11 of them. The median ratio in 1987 was 1.05 in 1987 and 1.17 in 2004. The absorbance/COD ratio during 1987–2004, on the other hand, is more stable. There are significant increases in two rivers and significant decrease in one river.  $[\text{SO}_4^{2-}]$  is negatively correlated to both absorbance/TOC (median  $r^2$  0.34) and COD/TOC (median  $r^2$  0.23). Flow is positively correlated to absorbance/TOC (median  $r^2$  0.30), but generally not to COD/TOC (median  $r^2$  0.04).

For the MLR models using flow and  $[\text{SO}_4^{2-}]$ , the residuals were checked for normality with the Shapiro–Wilk test. A  $P$ -value above 0.05 indicates that the

residuals are at least approximately normally distributed. For absorbance, this was the case for 26 of the 28 modelled rivers, for COD the  $P$ -value was above 0.05 for 25 of 28 rivers, and for TOC for 17 of 21 rivers.

## Discussion

In spite of the simple modelling approach, much of the interannual variability can be predicted by only two variables: flow and  $[\text{SO}_4^{2-}]$  (up to 76% for COD and TOC, and up to 88% for absorbance, Fig. 4). One should of course be careful about drawing conclusions from linear, empirical relationships. Nonlinear interactions and factors not considered in this analysis, such as atmospheric  $\text{CO}_2$  and nitrogen deposition may also manifest themselves in future OM patterns. Nonetheless, the high degree of variation explained in these rivers with a wide range of catchment characteristics over a large geographical area gives confidence that both flow and  $[\text{SO}_4^{2-}]$  are important controls.

There are strong indications that OM has increased since the late 1970s in most of the studied rivers (median total increase 65% for absorbance, 29% for COD). Both  $[\text{SO}_4^{2-}]$  and temperature have significant trends during most of the period, with decreasing  $[\text{SO}_4^{2-}]$  and increasing temperature. Thus, they should both potentially be able to statistically explain the linear increasing trend component of OM. The temperature, however, is also negatively correlated to the flow (Fig. 1), which is why temperature as a driver yields very low  $r^2$ -values, with negative relationships between temperature and OM for many rivers.  $[\text{SO}_4^{2-}]$  as a sole driver, on the other hand, yields a mean  $r^2$  of 0.33 for COD, and 0.52 for absorbance. Of particular value in this analysis, in contrast to most other trend studies of OM, is that the data records for  $[\text{SO}_4^{2-}]$ , absorbance and COD extends far enough back in time to include a period (1970–1976) when  $[\text{SO}_4^{2-}]$  in surface waters were still increasing in most of the rivers. The distinct difference in OM trends between rivers with high and low  $\text{SO}_4^{2-}$  levels in the 1970s (Fig. 3) also suggests that there is a mechanism linking  $\text{SO}_4^{2-}$  to change in the amount and/or quality of OM. Some of the studied rivers had very high  $[\text{SO}_4^{2-}]$  ( $>0.5 \text{ meq L}^{-1}$ ) during the 1970s. These rivers are situated below the highest postglacial coastline in areas in the east and southwest of Sweden. The most likely reason for the high levels of  $\text{SO}_4^{2-}$  for these is natural occurrence of sulphides in the soil, originating from marine sediments. During dry conditions (like in the middle of the 1970s), these can oxidize and enter the surface water as  $\text{SO}_4^{2-}$ . This can be considered as a kind of ‘natural acidification’. Since the dry period in the 1970s, and in combination with declining deposition,  $[\text{SO}_4^{2-}]$  has declined substantially in these rivers.

The  $\text{Fe}^{3+}$  ion can be a confounding factor when using absorbance as a measure of OM, because the ion is coloured. The ion binds strongly to humic compounds, and Fe has a significant positive correlation (at a 95% significance level) with both flow (16 of 23 rivers), and COD (21 of 23 rivers). Thus, Fe enhances the absorbance signal when OM concentrations are changing, which is one likely cause of the higher  $r^2$  values yielded for absorbance relative to flow, than for the other OM measures.

For TOC, the percentage increase during 1987–2004 is smaller than for either COD or absorbance. Therefore,  $[\text{SO}_4^{2-}]$  is seldom a good predictor for TOC concentrations. This is in contrast to studies in the United Kingdom (Evans *et al.*, 2005) and Finland (Vuorenmaa *et al.*, 2006), among others, where a larger TOC increase in that period has been observed, together with better correlations to  $[\text{SO}_4^{2-}]$ . There is a contrast between the behaviour of TOC, which is solely a measure of OM quantity, and COD and absorbance, which reflects both OM quantity and quality. Of the OM measures, absorbance has the strongest response to both flow and  $[\text{SO}_4^{2-}]$ , COD has the second strongest response, and TOC has the weakest response. As a consequence, the ratios absorbance/TOC and COD/TOC have a negative correlation to  $[\text{SO}_4^{2-}]$ , and the ratio absorbance/TOC also shows a positive correlation to flow. This implies that both the quality and the quantity of OM have trends related to sulphate deposition, and interannual fluctuations related to flow. The ratio absorbance/TOC is closely related to specific ultra-violet absorbance (SUVA), a measure of quality that is widely acknowledged as a measure for DOC aromaticity (Weishaar *et al.*, 2003). SUVA has a profound impact on properties such as biodegradability (Sachse *et al.*, 2001) and complex binding to metals (McKnight *et al.*, 1992). Thus, the quality changes noted in this study also need to be considered when evaluating the ecological significance of the factors influencing OM.

It might be argued that the variability in  $[\text{SO}_4^{2-}]$  and  $[\text{Cl}^-]$  associated with fluctuations in flow should be considered as a component of the hydrological driver. If so, flow normalization of these constituents can separate the driving forces of hydrology from  $[\text{SO}_4^{2-}]/[\text{Cl}^-]$  in runoff. The actual effect of the flow normalization on the results was not very large, however, because annual mean values are being considered.

Changes of land use may affect the amount of OM in runoff and confound the impact of external drivers. Regional scale changes in land use, however, have been relatively small during the period. The proportion of productive forestry areas declined from 57.2% in 1970 to 54.7% in 1992, and then increased again to 55.9% in 2004 (Riksskogstaxeringen, 2005). The proportion of arable

land in Sweden has declined from 9.2% in 1970 to 8.4% in 2004, and the area of wetlands has declined from 12.2% in 1970 to 10.9% in 2004 (SCB, 2004). Because all catchments in the study are at least 200 km<sup>2</sup>, they are not likely to be significantly affected by intermittent events of limited spatial extent, such as clear cutting of forests.

Much of the concern about OM in the recent literature has focussed on trends, and the importance of long-term increases for aquatic ecosystems and biota. Even if the long-term increases in OM concentrations are considerable, the interannual variability caused by variations in flow is often even larger. For example, in the 5-year period between 1976 (a dry year) and 1981 (a wet year), the mean increase in absorbance was 96%, and 38% for COD. This is a larger increase than that observed over the entire 35-year study period. It is also possible to find two consecutive years where OM changes more than the average change during the whole period for 16 of the rivers for COD, and for 13 of the rivers for absorbance. Hence, the extremes that both aquatic biota and society must contend with are hydrologically driven, and will likely continue to be so. There is also an important seasonal and episodic dynamic in the OM concentrations of many rivers (Schiff *et al.*, 1998) that has not been addressed in this study, or most long-term analyses.

Several recent studies examining drivers of stream/riverine OM trends have not found flow to be an important factor (Evans *et al.*, 2006; Vuorenmaa *et al.*, 2006). In the case of the UK studies, this may be due to the predominance of peats in many of the catchments. Peat soils can have a negative flow–OM relationship (Gorham *et al.*, 1998; Mulholland, 2003), whereas the more extensive areas of forest soils tend to have positive flow–OM relationships (Hinton *et al.*, 1997). Because different parts of the landscape mosaic of soils can have such different patterns of OM output in relation to flow (Laudon *et al.*, 2004; Temnerud & Bishop, 2005), the composition of that mosaic will affect the importance of flow seen at the catchment scale. Higher proportions of forested mineral soils in the larger catchments of this study could thus be expected to show flow driving OM more consequentially than in catchments with more of a balance between wetlands and forest soils with their contrasting flow–OM relationships. Given how few headwaters are actually monitored (Temnerud & Bishop, 2005), extrapolations from small catchments are particularly sensitive to how well the sample represents the region. The catchments reported here are orders of magnitude larger than those analysed in many other regional studies, and are thus more spatially integrated representatives of how the four candidate drivers influence regional OM patterns.

Because the dramatic decline in SO<sub>4</sub><sup>2-</sup> deposition across the western world is not expected to continue, SO<sub>4</sub><sup>2-</sup> will not be driving OM much further upwards. The increase in OM associated with SO<sub>4</sub><sup>2-</sup> decline is also better characterized as a relaxation of OM suppression associated with anthropogenic SO<sub>4</sub><sup>2-</sup> deposition (Clark *et al.*, 2005; Evans *et al.*, 2006). Hydrology, however, will continue to drive variability in OM concentrations.

In Scandinavia, climate change is predicted to have increased precipitation by 10–25% in the period 2071–2100, relative to the reference period of 1961–1990 (Räisänen *et al.*, 2004). However, the expected increase in temperature will cause increasing evapotranspiration as well, resulting in a dampened increase, or even decrease, in runoff. The predicted scenario is an increase in runoff of 5% in northern Sweden, a decrease in runoff of 10% in southern Sweden, whereas runoff remains unchanged in central Sweden (Mattsson & Rummukainen, 1998). Using the empirical relationship between flow and the different measures of OM, this would result in a COD increase of about 1.5% and an absorbance increase of 3% in northern Sweden. In southern Sweden, a decrease of 1.5–4% in COD and 3–7% in absorbance could be expected. This is not much compared with the shorter term fluctuations between years and within years. Thus, it is the shorter duration excursions in OM (hours to years) that will likely be of most concern for water resources and the aquatic biota in Scandinavia and similar regions of the boreal zone in the decades ahead.

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### References

- Clark JM, Chapman PJ, Adamson JK, Lane SN (2005) Influence of drought-induced acidification on the mobility of dissolved organic carbon in peat soils. *Global Change Biology*, **11**, 791–809.
- Cleveland WS, Devlin SJ (1988) Locally weighted regression – an approach to regression-analysis by local fitting. *Journal of the American Statistical Association*, **83**, 596–610.
- Eikebrokk B, Vogt RD, Liltved H (2004) NOM increase in Northern European source waters: discussion of possible causes and impacts on coagulation/contact filtration processes. *Water Science and Technology: Water Supply*, **4**, 47–54.



- Evans CD, Chapman PJ, Clark JM, Monteith DT, Cresser MS (2006) Alternative explanations for rising dissolved organic carbon export from organic soils. *Global Change Biology*, **12**, 2044–2053.
- Evans CD, Monteith DT, Cooper DM (2005) Long-term increases in surface water dissolved organic carbon: observations, possible causes and environmental impacts. *Environmental Pollution*, **137**, 55–71.
- Forsberg C (1992) Will an increased greenhouse impact in Fennoscandia give rise to more humic and colored lakes. *Hydrobiologia*, **229**, 51–58.
- Freeman C, Evans CD, Monteith DT, Reynolds B, Fenner N (2001) Export of organic carbon from peat soils. *Nature*, **412**, 785.
- Freeman C, Fenner N, Ostle NJ *et al.* (2004) Export of dissolved organic carbon from peatlands under elevated carbon dioxide levels. *Nature*, **430**, 195–198.
- Gadmar TC, Vogt RD, Osterhus B (2002) The merits of the high-temperature combustion method for determining the amount of natural organic carbon in surface freshwater samples. *International Journal of Environmental Analytical Chemistry*, **82**, 451–461.
- Gorham E, Underwood JK, Janssens JA, Freedman B, Maass W, Waller DH, Ogden JG (1998) The chemistry of streams in southwestern and central Nova Scotia, with particular reference to catchment vegetation and the influence of dissolved organic carbon primarily from wetlands. *Wetlands*, **18**, 115–132.
- Helsel DR, Hirsch RM (1992) Statistical methods in water resources. *Studies in Environmental Science*. Elsevier Science B.V., Amsterdam.
- Hinton MJ, Schiff SL, English MC (1997) The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. *Biogeochemistry*, **36**, 67–88.
- Hongve D, Riise G, Kristiansen JF (2004) Increased colour and organic acid concentrations in Norwegian forest lakes and drinking water – a result of increased precipitation? *Aquatic Sciences*, **66**, 231–238.
- Ivarsson H, Jansson M (1994) Regional variation of dissolved organic-matter in running waters in central northern Sweden. *Hydrobiologia*, **286**, 37–51.
- Kalbitz K, Solinger S, Park JH, Michalzik B, Matzner E (2000) Controls on the dynamics of dissolved organic matter in soils: a review. *Soil Science*, **165**, 277–304.
- Laudon H, Köhler S, Buffam I (2004) Seasonal TOC export from seven boreal catchments in northern Sweden. *Aquatic Sciences*, **66**, 223–230.
- Mackereth FJH (1955) Ion-exchange procedures for the estimation of (I) total ionic concentration, (II) chlorides and (III) sulphates in natural waters. *Mitteilungen der IVL*, **4**, 1–16.
- Mattsson T, Kortelainen P, Raike A (2005) Export of DOM from boreal catchments: impacts of land use cover and climate. *Biogeochemistry*, **76**, 373–394.
- Mattsson J, Rummukainen M (1998) *Växthuseffekten och klimatet i Norden – en översikt. Meteorologi*. Publication No. 88. Rossby Center, SMHI.
- McKnight DM, Bencala KE, Zellweger GW, Aiken GR, Feder GL, Thorn KA (1992) Sorption of dissolved organic carbon by hydrous aluminum and iron oxides occurring at the confluence of deer creek with the Snake River, Summit County, Colorado. *Environmental Science and Technology*, **26**, 1388–1396.
- Monteith DT, Stoddard JL, Evans CD *et al.* (2007) Dissolved organic carbon trends result from changes in atmospheric deposition chemistry. *Nature*, **450**, 537–540.
- Mulholland PJ (2003) Large-scale patterns in dissolved organic carbon concentration, flux, and sources. In: *Aquatic Ecosystems: Interactivity of Dissolved Organic Matter* (eds Findlay S, Sinsabaugh R), pp. 139–159. Elsevier Science, San Diego.
- Pregitzer KS, Zak DR, Burton AJ, Ashby JA, MacDonald NW (2004) Chronic nitrate additions dramatically increase the export of carbon and nitrogen. *Biogeochemistry*, **68**, 179–197.
- Räsänen J, Hansson U, Ullerstig A *et al.* (2004) European climate in the late twenty-first century: regional simulations with two driving global models and two forcing scenarios. *Climate Dynamics*, **22**, 13–31.
- Riksskogstaxeringen (2005) Landarealen fördelad på ägoslag [online]. Available from: <http://www-riksskogstaxeringen.slu.se/Resultat/agoslag.htm> [cited 10 April 2007].
- Roulet N, Moore TR (2006) Environmental chemistry – browning the waters. *Nature*, **444**, 283–284.
- Sachse A, Babenzien D, Ginzel G, Gelbrecht J, Steinberg CEW (2001) Characterization of dissolved organic carbon (DOC) in a dystrophic lake and an adjacent fen. *Biogeochemistry*, **54**, 279–296.
- SCB (2004) *Markanvändningen allmänt*. In: *Markanvändningen i Sverige*, 4th ed. pp. 19–66. Statistiska Centralbyrån, Sweden.
- Schiff S, Aravena R, Mewhinney E, Elgood R, Warner B, Dillon P, Trumbore S (1998) Precambrian shield wetlands: hydrologic control of the sources and export of dissolved organic matter. *Climatic Change*, **40**, 167–188.
- Schindler DW (1998) A dim future for boreal waters and landscapes. *Bioscience*, **48**, 157–164.
- SLU (2007) Analysmetoder [online]. Available from: [http://info1.ma.slu.se/ma/www\\_ma.acgi\\$Analysis?ID=AnalysisList](http://info1.ma.slu.se/ma/www_ma.acgi$Analysis?ID=AnalysisList) [cited 15 May 2007].
- Stålnacke P, Grimvall A (2001) Semiparametric approaches to flow normalization and source apportionment of substance transport in rivers. *Environmetrics*, **12**, 233–250.
- Temnerud J, Bishop K (2005) Spatial variation of streamwater chemistry in two Swedish boreal catchments: implications for environmental assessment. *Environmental Science and Technology*, **39**, 1463–1469.
- Vuorenmaa J, Forsius M, Mannio J (2006) Increasing trends of total organic carbon concentrations in small forest lakes in Finland from 1987 to 2003. *Science of the Total Environment*, **365**, 47–65.
- Weishaar JL, Aiken GR, Bergamaschi BA, Fram MS, Fujii R, Mopper K (2003) Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science and Technology*, **37**, 4702–4708.
- Weyhenmeyer GA, Willén E, Sonesten L (2004) Effects of an extreme precipitation event on water chemistry and phytoplankton in the Swedish Lake Malaren. *Boreal Environment Research*, **9**, 409–420.
- Wilander A (1988) Organiskt material i vatten – en jämförelse av resultat från olika analysmetoder. *Vatten*, **44**, 217–224.
- Worrall F, Burt TP (2007) Flux of dissolved organic carbon from UK rivers. *Global Biogeochemical Cycles*, **21**, GB1013, doi: 10.1029/2006GB002709.