

# Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry

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Several hypotheses have been proposed to explain recent, widespread increases in concentrations of dissolved organic carbon (DOC) in the surface waters of glaciated landscapes across eastern North America and northern and central Europe<sup>1–3</sup>. Some invoke anthropogenic forcing through mechanisms related to climate change<sup>3–5</sup>, nitrogen deposition<sup>6</sup> or changes in land use<sup>7</sup>, and by implication suggest that current concentrations and fluxes are without precedent. All of these hypotheses imply that DOC levels will continue to rise, with unpredictable consequences for the global carbon cycle. Alternatively, it has been proposed that DOC concentrations are returning toward pre-industrial levels as a result of a gradual decline in the sulphate content of atmospheric deposition<sup>8–10</sup>. Here we show, through the assessment of time series data from 522 remote lakes and streams in North America and northern Europe, that rising trends in DOC between 1990 and 2004 can be concisely explained by a simple model based solely on changes in deposition chemistry and catchment acid-sensitivity. We demonstrate that DOC concentrations have increased in proportion to the rates at which atmospherically deposited anthropogenic sulphur and sea salt have declined. We conclude that acid deposition to these ecosystems has been partially buffered by changes in organic acidity and that the rise in DOC is integral to recovery from acidification. Over recent decades, deposition-driven increases in organic matter solubility may have increased the export of DOC to the oceans, a potentially important component of regional carbon balances<sup>11</sup>. The increase in DOC concentrations in these regions appears unrelated to other climatic factors.

A number of national monitoring programmes, designed to assess the effects of acid emission reductions on acid-sensitive lakes and streams, have reported increases in DOC concentrations over the past two decades<sup>2,4,9</sup>. Many monitoring networks were initiated in the late 1980s, and our analysis focuses on the period 1990–2004 to maximize geographical coverage. Over this period, sulphur deposition fell sharply in most regions<sup>2</sup>. Simultaneously, sea salt deposition to some coastal regions of northwestern Europe declined, following prolonged exceptionally stormy conditions in the early 1990s (ref. 12).

The geographical extent of recorded DOC increases suggests a common dominant driver, and highlights the need for a large-scale inter-regional analysis of time series data<sup>1</sup>. We examined the spatial distribution of DOC trends in data collected in glaciated regions of six North European and North American countries, and assessed the mechanisms capable of explaining observed patterns.

Our trend results are consistent with previous reports of DOC increases in surface waters on glaciated, acid-sensitive terrain in Europe and North America (Fig. 1; also see Supplementary Information). Upward slopes ( $n = 363$ ) outnumbered downward slopes ( $n = 139$ ), and 88% of significant trends ( $P < 0.05$ ) were positive. Upward slopes were most frequently significant in the Southern Nordic region (below 62° latitude), in the UK, and in the northeastern USA. Between 1990 and 2004, sulphur and/or chloride deposition declined in these regions as a result of reductions in sulphur emissions (all areas) and in the severity of coastal storms, respectively. The majority of DOC records in the northern Nordic region, and in Ontario/Quebec, also showed positive slopes, although fewer of these were significant ( $P < 0.05$ ). Atlantic Canada was the only region with little evidence of increasing DOC.

We found that relative change in DOC (that is, DOC change per year as a percentage of the site median, or % $\Delta$ DOC) was strongly and inversely related to change in both sulphate concentration ( $\Delta$ SO<sub>4</sub><sup>2–</sup>) and chloride concentration ( $\Delta$ Cl<sup>–</sup>) ( $n = 522$ ; Fig. 2). Surface water SO<sub>4</sub><sup>2–</sup> and Cl<sup>–</sup> concentrations in these northern ecosystems are generally highly correlated with concentrations of these ions in deposition, and can serve as surrogates for site-specific measurements of SO<sub>4</sub><sup>2–</sup> and Cl<sup>–</sup> deposition<sup>13</sup> (see Methods Summary). While falling SO<sub>4</sub><sup>2–</sup> dominated most records, large DOC increases occurred in some coastal locations where  $\Delta$ SO<sub>4</sub><sup>2–</sup> was small, provided that  $\Delta$ Cl<sup>–</sup> was strongly downward. Increased sea salt deposition appeared to be critical in explaining the unusual DOC declines in some parts of Atlantic Canada (Fig. 1).

To explore potential factors affecting the % $\Delta$ DOC, we performed a forward-selection stepwise regression that included variables representing both trend results (annual slopes) and median values of key chemical and regional temperature parameters (see Methods Summary).  $\Delta$ SO<sub>4</sub><sup>2–</sup> and  $\Delta$ Cl<sup>–</sup> were selected, along with median non-marine Ca<sup>2+</sup> + Mg<sup>2+</sup> concentration (CaMg\*, representing catchment sensitivity to acidification), and an interaction term ( $\Delta$ Cl<sup>–</sup>  $\times$  CaMg\*) (Table 1). All four variables were highly significant, and explained 39.3% of the variance in % $\Delta$ DOC. Given the uncertainties surrounding trend estimation, and the influence of inevitable local and sub-regional factors on DOC trends at individual sites, the explanatory power of this single multi-regional model is considerable.

Residuals from our model support the idea that recent widespread DOC changes are related to changes in the atmospheric deposition of SO<sub>4</sub><sup>2–</sup> and Cl<sup>–</sup> across large areas (Fig. 3). The UK was the only region where the median of residuals was significantly different from zero, perhaps because the true trend in SO<sub>4</sub><sup>2–</sup> deposition for UK sites was

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underestimated (owing to short-term adsorption of  $\text{SO}_4^{2-}$  during heightened sea salt deposition in the early 1990s in this region, the most maritime in the data set<sup>12</sup>). The model can account entirely for the average slight negative DOC trend in Atlantic Canada, the small average increases in the northeastern USA, Ontario/Quebec and northern Nordic regions and the large average increase in the southern Nordic region. The approximately even distribution of residuals around the median for each region suggests that much of the residual variance is of a local or random, rather than systematic, nature (Fig. 3).

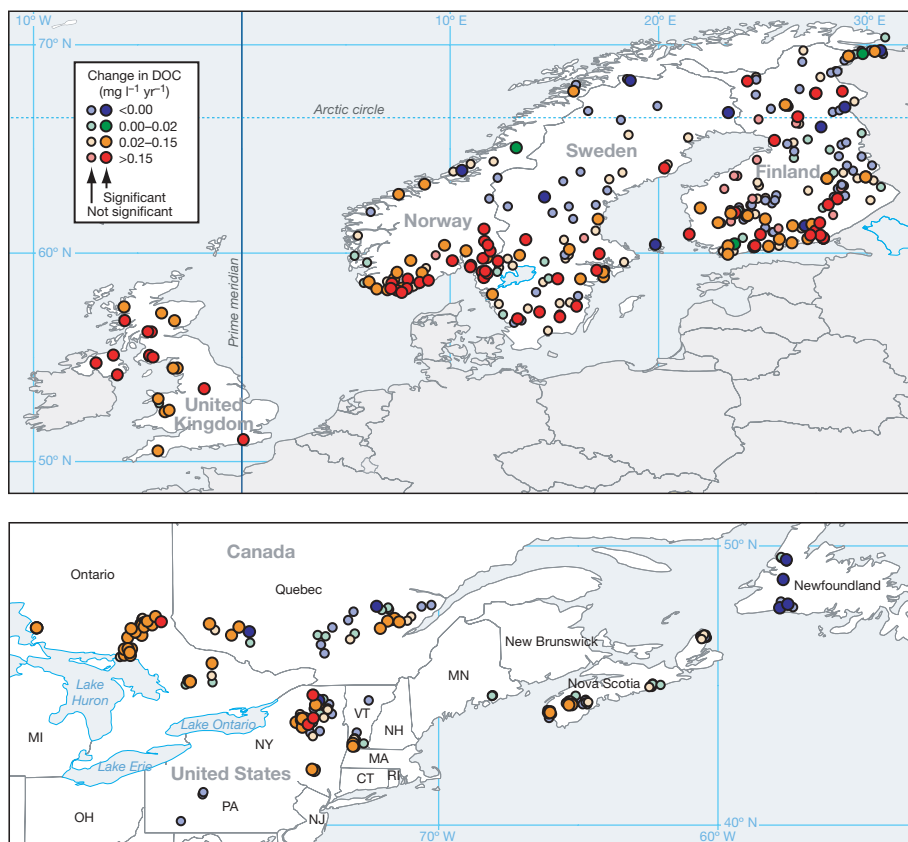
A number of other factors are known to influence short-term variation in DOC concentration in surface waters, and some of those that have undergone recent change have been proposed to explain long-term DOC trends<sup>3–7,14,15</sup>. None of these factors, however, exhibit spatial patterns that are consistent with the patterns of DOC change that we observe (Fig. 1 and Supplementary Information). For example, recent data from rivers in the UK<sup>16</sup>, the eastern USA<sup>17</sup>, Norway<sup>18</sup>, Canada<sup>19</sup> and Finland<sup>20</sup> provide no evidence for trends in seasonal or annual hydrology that are spatially consistent with the distribution of DOC trends. We could not use runoff chemistry to assess the influence of changing nitrogen (N) deposition on DOC trends, because atmospheric N is retained strongly in most catchments and is thus non-conservative. Although N is certainly accumulating in many ecosystems, both the amounts of N deposition, and temporal trends in N deposition and runoff, are highly variable across our sites<sup>21</sup>. In our data set, only 28 sites showed significant ( $P < 0.05$ ) increases in nitrate concentration (indicative of possible nitrogen saturation), 100 showed declines and 394 showed no trend. We found no indication of trends in seasonal or annual air temperatures across northern Europe during the period 1990–2004, with the exception of Scotland (autumn only) and northern and eastern Finland (summer only). Upward temperature trends were more widespread in eastern North America, but occurred in regions where there was no dominant DOC tendency. Although  $\text{CO}_2$  concentrations are increasing globally, they cannot simultaneously explain both the upward and downward trends in DOC we observe in different regions. Finally, there have been no consistent land-use changes across all regions.

Changes in the chemistry of atmospheric deposition, therefore, provided the only regionally consistent explanation for widespread upward trends in surface water DOC concentrations. A comparison of the relative effects of non-marine (that is, anthropogenic)  $\text{SO}_4^{2-}$  and the combined effects of  $\text{Cl}^-$  and marine  $\text{SO}_4^{2-}$ , using the coefficients from our model, showed that, on average, the reduction in anthropogenic  $\text{SO}_4^{2-}$  was responsible for >85% of the total anion effect on  $\Delta\text{DOC}$  in all regions other than the UK (where anthropogenic and marine effects were similar) and Atlantic Canada (where marine effects dominated) (see Supplementary Information). However, the selection of  $\Delta\text{Cl}^-$  in the model, with a coefficient of similar magnitude to that for  $\Delta\text{SO}_4^{2-}$ , is suggestive of common soil processes.

Atmospheric deposition can affect soil organic matter (SOM) solubility through at least two mechanisms—by changing either the acidity of soils or the ionic strength of soil solutions, or both. Acid deposition and sea salt can exert similar short-term effects on both processes. Krug and Frink<sup>22</sup> originally proposed that increasing the pH of base-poor soils should increase SOM solubility. Although their premise—that surface water acidification would be minimized by the resulting substitution of mineral acids for organic acids—has been widely disproved, SOM solubility has since been linked to soil pH in laboratory<sup>23,24</sup> and field<sup>23,25</sup> studies; soil equilibrium models<sup>26</sup> now include the pH dependence of SOM solubility. Soil pH also determines the solubility of aluminium which, when released during the process of soil acidification, can bind with organic molecules, neutralising high-affinity binding-sites and thereby triggering SOM coagulation<sup>27</sup>.

Declining acid deposition and, in a minority of sites, a decline in the frequency and intensity of sea salt episodes may affect DOC concentrations both directly, by increasing soil pH, and indirectly, by reducing aluminium mobilisation. The selection of  $\text{CaMg}^*$ , an indicator of acid sensitivity in our multiple regression model (Table 1), provides some support for this soil pH/DOC solubility mechanism.

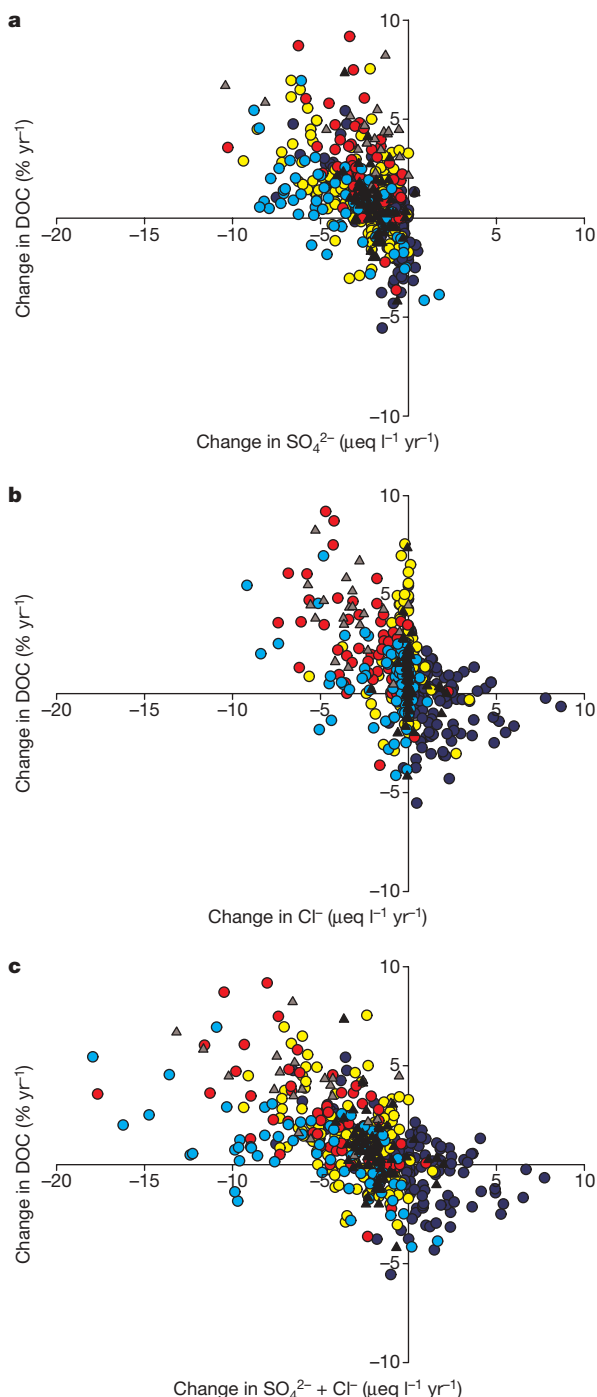
A second mechanism involves the effect of ionic strength on the coagulation of DOC. Decreasing inputs of acidic deposition or sea salt should lead to lower concentrations of a suite of multivalent ions found in soil solution—including  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and aluminium—that



**Figure 1 | Trends in dissolved organic carbon ( $\text{mg l}^{-1} \text{yr}^{-1}$ ).** Data are shown for monitoring sites on acid-sensitive terrain in Europe (upper panel) and North America (lower panel) for the period 1990–2004.

exert a large influence on ionic strength. Previous studies have shown that increasing the ionic strength of soil solutions reduces the rate of DOC flux<sup>26,28</sup>; conversely, a reduction in ionic strength (for example, through decreasing atmospheric deposition) should lead to a DOC increase. The selection of CaMg\* in our model may also be relevant here, because the ionic strength of the soil solution in catchments where CaMg\* is low should be more sensitive to change in the deposition of these ions.

Evidence for our conclusions thus derives from three lines of support: (1) a plausible mechanism; (2) experimental studies showing



**Figure 2 | Relationship between % $\Delta$ DOC,  $\Delta$ SO<sub>4</sub><sup>2-</sup> and  $\Delta$ Cl<sup>-</sup> and the equivalent sum of  $\Delta$ SO<sub>4</sub><sup>2-</sup> and  $\Delta$ Cl<sup>-</sup>, used as surrogates for changes in atmospheric deposition. a,  $\Delta$ SO<sub>4</sub><sup>2-</sup>; b,  $\Delta$ Cl<sup>-</sup>; c,  $\Delta$ SO<sub>4</sub><sup>2-</sup> and  $\Delta$ Cl<sup>-</sup>. Symbols represent data from Canada (dark blue circles), Finland (yellow circles), Norway (red circles), Sweden (light blue circles), the UK (grey triangles) and the USA (black triangles).**

**Table 1 | Results of stepwise multiple regression for % $\Delta$ DOC**

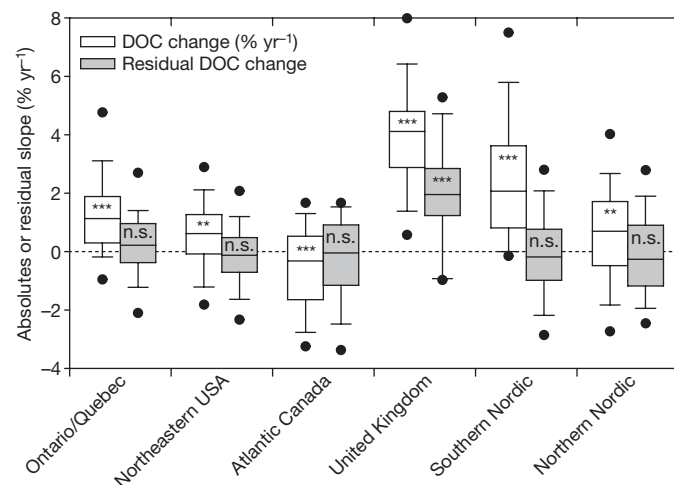
Variable	Estimate	P	Cumulative R <sup>2</sup>
Intercept	0.250	0.0004	NA
Change in SO <sub>4</sub> <sup>2-</sup> (μeq l <sup>-1</sup> yr <sup>-1</sup> )	-0.557	<0.0001	0.237
Median CaMg* (μeq l <sup>-1</sup> )	-0.005	<0.0001	0.316
Change in Cl <sup>-</sup> (μeq l <sup>-1</sup> yr <sup>-1</sup> )	-0.504	<0.0001	0.360
Median CaMg* (μeq l <sup>-1</sup> ) × change in Cl <sup>-</sup> (μeq l <sup>-1</sup> yr <sup>-1</sup> )	0.0033	<0.0001	0.393

See Methods Summary. Estimates for intercept and slope of individual relationships are for the final three variable plus one interaction model. NA, not applicable. μeq, microequivalents. \*Sea-salt-corrected divalent cation concentration.

that our proposed mechanism is capable of causing the observed DOC response; and (3) temporal and spatial coherence of both the 'cause' (changing atmospheric deposition) and the 'effect' (changing DOC levels). Our results provide the first clear, large-scale demonstration that DOC concentrations are sensitive to changes in acid deposition, and, therefore, that declining surface water acidity (mediated by decreasing acid deposition) is being partially offset by increasing organic acidity. Furthermore, they suggest that DOC fluxes from these regions to the oceans may be returning to levels more typical of pre-industrial times.

In maritime northwestern Europe, both SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> have fallen over the 1990–2004 period, but for unrelated reasons. Sea salt deposition varies due to meteorological factors that affect Atlantic storminess, such as the North Atlantic Oscillation<sup>12</sup>, producing roughly decadal oscillations. Trends in SO<sub>4</sub><sup>2-</sup> deposition, on the other hand, have operated over much longer timescales and are similar to those in other regions covered by this study. Rates of sulphur deposition began rising in the mid- to late 1800s, peaked in the 1970s, and have subsequently fallen. At timescales greater than decades, long-term trends in DOC will be controlled by changes in sulphate deposition, even in regions subject to large sea salt inputs.

Although acid deposition has affected large parts of Europe and North America, it has not been a global phenomenon. These findings emphasize, therefore, that evidence of rising DOC in these (well-studied) areas should not be misconstrued as evidence of rising DOC



**Figure 3 | Distributions of % $\Delta$ DOC and residuals from multiple regression, by region.** Boxplots are of regional distributions of  $\Delta$ %DOC per year (unshaded boxes) and residuals calculated from a multiple regression predicting  $\Delta$ %DOC from  $\Delta$ SO<sub>4</sub><sup>2-</sup>,  $\Delta$ Cl<sup>-</sup>, median CaMg\* concentration and the interaction term  $\Delta$ Cl<sup>-</sup> × CaMg\* (grey boxes). Symbols within boxes indicate significance of the one-sample median test of  $H_0$ : median = 0 (\*\*\* $P$  < 0.001; \*\* $P$  < 0.01; not significant  $P$  > 0.05). Boundaries of boxes indicate interquartile range (25th to 75th percentiles) and median value (midline); whiskers indicate 10th and 90th percentiles and symbols indicate 5th and 95th percentiles. Residual values centre around zero for all regions, with the possible exception of the UK, indicating that the regression model built on all data reliably explains the tendency for  $\Delta$ %DOC concentrations to deviate from zero in the separate regions.



in unmonitored waters globally. They also suggest that threats of widespread destabilization of terrestrial carbon reserves by gradual rises in air temperature or CO<sub>2</sub> concentration<sup>3–5</sup> may have been overstated. There is, however, a clear need for closer integration of research into pollutant and climatic impacts on terrestrial carbon dynamics. An improved understanding of the roles of both, and their interactions, is required to predict future surface water quality accurately, and to determine crucially important linkages between climate and the carbon cycle.

## METHODS SUMMARY

Water chemistry data were collated from several regional and national monitoring initiatives for the period 1990–2004. Records represent mostly headwater lakes and lower-order streams that are largely free of local disturbance, other than potential effects of forestry and rough grazing practices. Data were analysed for trends by the Mann–Kendall test<sup>29</sup>, with slopes estimated by the Sen estimator<sup>30</sup>.

Site-specific deposition estimates were not available for most of the surface water monitoring sites, so we used changes in measured surface water concentrations of SO<sub>4</sub><sup>2–</sup> (ΔSO<sub>4</sub><sup>2–</sup>) and Cl<sup>–</sup> (ΔCl<sup>–</sup>), as deposition surrogates. Inputs and outputs of SO<sub>4</sub><sup>2–</sup> rarely balance precisely, but in younger (that is, glaciated) northern ecosystems the two are generally highly correlated<sup>13</sup>.

Regional trends in seasonal (that is, mean December–February, March–May, June–August and September–November) and annual air temperature were determined from CRUTEM2 simulated air temperature anomaly data from the Climate Research Unit, University of East Anglia (<http://www.cru.uea.ac.uk/cru/data/tem2/>). These data are compiled in a 5° × 5° global grid, so several monitoring sites may be associated with a single, grid-based estimate of temperature change over the 1990–2004 time period relative to the 1961–1990 average.

To determine factors influencing %ADOC at the regional scale, we conducted a stepwise multiple regression using, for each site, both trend results (annual slopes) and median values of key chemical variables (SO<sub>4</sub><sup>2–</sup>, non-marine SO<sub>4</sub><sup>2–</sup>, Cl<sup>–</sup>, NO<sub>3</sub><sup>–</sup>, H<sup>+</sup>, acid-neutralizing capacity, Gran alkalinity, base cations, CaMg\* and aluminium), together with slopes for annual and seasonal temperature anomalies for the representative 5° grid square for each site. In an initial run, ΔSO<sub>4</sub><sup>2–</sup>, ΔCl<sup>–</sup> and CaMg\* were the only variables selected. Because sites with declining ΔSO<sub>4</sub><sup>2–</sup> and ΔCl<sup>–</sup> dominated the data set, the negative coefficient for CaMg\* (Table 1) suggested that the DOC response to declining anion concentrations was greatest in the most acid-sensitive systems. We therefore introduced an additional interaction term (ΔCl<sup>–</sup> × CaMg\*) to account for the potentially dampening effect of larger base cation concentrations on negative DOC trends at a minority of sites at which ΔCl<sup>–</sup> had increased.

**Full Methods** and any associated references are available in the online version of the paper at [www.nature.com/nature](http://www.nature.com/nature).

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**Supplementary Information** is linked to the online version of the paper at [www.nature.com/nature](http://www.nature.com/nature).

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**Author Contributions** D.T.M. and J.L.S. formulated the working hypothesis and analysed and interpreted the trend data. C.D.E. and H.A.d.W. contributed to the development of the hypothesis, assisted in the interpretation of the data, provided additional text and edited the manuscript. M.F., T.H., A.W., B.L.S., D.S.J., B.K. and J. Vuorenmaa provided data and commented on the text. J.K. provided advice and ideas on processes and contributed data from the Czech Republic (not included in the final analysis due to number and length of time series) consistent with the hypothesis. J. Vesely contributed advice, ideas and data in the early stages of development of our work.

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## METHODS

Data were drawn from a number of monitoring programmes with varying sampling protocols. Data for streams were accepted only if these represented multiple samples per year, while single annual samples for lakes were included provided these were collected in the same season for individual lakes. Analysis was restricted to sites with, at a minimum, annual measurements for ten of the 15 years between 1990 and 2004. Data for sites with more frequent sampling were reduced to one representative observation per year, by estimating annual mean values.

Given the multiple sources, all data were subjected to rigorous quality assurance. In addition to standard quality assurance procedures (for example, charge balance, calculated versus measured conductivity), we also examined the data for evidence of road salt inputs (by comparing  $\text{Cl}^-$  concentration to distance from the coast), or catchment sources of  $\text{SO}_4^{2-}$ , either of which could produce anomalous trends. We eliminated a handful of sites ( $n = 15$ ) for which the  $\text{SO}_4^{2-}$  trends could not be attributed to changing deposition (that is, the surface water  $\Delta\text{SO}_4^{2-}$  was more than three times the estimated deposition  $\Delta\text{SO}_4^{2-}$ ) and data from sites on older soils (for example, the southern Appalachian region of the US) where high levels of  $\text{SO}_4^{2-}$  adsorption lead to non-conservative behaviour. We also restricted our analysis to sites where DOC concentrations were sufficient to allow reliable quantification of trends; sites with median DOC concentrations of  $<1 \text{ mg l}^{-1}$  were excluded from our analyses. Our final data set comprised estimates of trends and mean concentrations for chemical and air temperature parameters for 522 sites.

To determine the relative effects of anthropogenic and marine deposition factors on  $\%\Delta\text{DOC}$  in our model, we first estimated the change in non-marine and marine sulphate (that is,  $\Delta\text{xSO}_4^{2-}$  and  $\Delta\text{mSO}_4^{2-}$ ) at each site using a sea-salt-correction factor, so that:  $\Delta\text{mSO}_4^{2-} = \Delta\text{Cl}^- \times 0.104$  and  $\Delta\text{xSO}_4^{2-} = \Delta\text{SO}_4^{2-} - \Delta\text{mSO}_4^{2-}$ . The effects of changing anthropogenic and marine anions on DOC were then determined from the model coefficients:

$$\%\Delta\text{DOC}(\text{anthropogenic}) = -0.557\Delta\text{xSO}_4^{2-}$$

$$\%\Delta\text{DOC}(\text{marine induced}) = -0.557\Delta\text{mSO}_4^{2-} - 0.504\Delta\text{Cl}^- + 0.0033\Delta\text{Cl}^- \times \text{CaMg}^*$$

Results, in the form of mean effects on  $\%\Delta\text{DOC}$  per region, are provided in Supplementary Table 5.