Increasing Dissolved Organic Carbon Redefines the Extent of Surface Water Acidification and Helps Resolve a Classic Controversy

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Concentrations of organic acids in freshwaters have increased significantly during recent decades across large parts of Europe and North America. Different theories of the causes (e.g., recovery from acidification, climate change, land use) have different implications for defining the preindustrial levels for dissolved organic carbon (DOC), which are crucial for assessing acidification and other aspects of water quality. We demonstrate this by classifying the acidification status of 66 lakes with long-term observations, representative of about 12,700 acid-sensitive lakes in nemoral and boreal Sweden. Of these lakes, 47% are classified as significantly acidified ($\Delta pH \geq 0.4$), assuming preindustrial DOC levels were equal to those observed in 1990. But if, instead, the higher DOC levels observed in 2009 define preindustrial conditions, half as many lakes are acidified (24%). This emphasizes the need to establish reference levels for DOC and casts new light on the classic controversy about natural versus anthropogenic acidification.

Keywords: reference conditions, water quality assessment, DOC increase, organic acids, recovery from acidification

Acidification caused by acid precipitation has been, and remains, a major environmental issue because of its life-threatening effects on biota, its global spread, and the prolonged recovery period associated with it. International cooperation to reduce the precursors of acid precipitation has provided a textbook example of how society can address a complex environmental pollution problem with support from science (Sundqvist et al. 2002). A key step in that success was the achievement of a broad scientific consensus that acid precipitation was a serious threat to ecosystems in sensitive regions. That consensus was built during two decades of scientific research starting with the first United Nations conference on the environment in 1972 and continuing to 1990 with the conclusion of major research programs in Europe (the Surface Water Acidification Programme) and in the United States (the National Acid Precipitation Assessment Program).

Reaching consensus took time because of controversy about the connection between acid emissions and terrestrial as well as aquatic acidification. Initially, there was a need to establish both empirical and theoretical bases for resolving conflicting viewpoints. One of the major challenges to the concept of acid precipitation leading to the acidification of surface waters was presented by Krug and Frink (1983), who questioned the link between acid rain and freshwater acidification, arguing that it was, rather, changes in land use that caused the observed declines in pH. One of their key arguments was that anthropogenic sulfate merely replaced the organic acidity in surface waters, with little or no change in pH. Many authors subsequently argued that acid precipitation did acidify surface waters (Van Breemen et al. 1984, Gorham et al. 1986, Brakke et al. 1987) and also increased concentrations of inorganic aluminum, which is particularly toxic to fish.

To test the contention that organic acidity was replaced by anthropogenic acidity, artificial acidification and recovery experiments have been conducted, with various and sometimes contradictory results. Wright (1989) and Hedin and colleagues (1990) found no effect from acidification on dissolved organic carbon (DOC) concentrations, whereas Schindler and colleagues (1992) found that experimental acidification to a pH below 5 caused DOC to decrease. A paleolimnological study (Davis et al. 1985) partly supported the claims of Krug and Frink (1983). Driscoll and colleagues (1989) also acknowledged that Krug and Frink (1983) were partly right, in that strong mineral acids did seem to suppress organic acidity to some extent, but not enough to completely mitigate the harmful effects from acid rain.

The widespread increase in the concentration of DOC observed in some regions of Northern Europe and North America provides a basis for reexamining the issue of DOC reference levels in acidification assessment. Although the

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cause of this decadal trend is still debated, reduced acid deposition and the subsequent recovery from acidification have been proposed as an explanation in several studies (Monteith et al. 2007, Haaland et al. 2010). Better models for representing the acidity of DOC have also made it possible to quantify the contributions of organic acids to the total acidity (Hruška et al. 2003). Several previous studies have examined how much the buffering by organic acids has retarded the recovery in pH (Driscoll et al. 2003, Evans et al. 2008, Erlandsson et al. 2010), but in none of these has the issue of how DOC has influenced acidification been fully addressed, because the preindustrial reference conditions against which anthropogenic acidification is measured have not been considered.

Significance of DOC reference levels for acidification assessments

According to the European Union Water Framework Directive, ecological disturbances should be defined by comparison with a reference condition that represents the undisturbed state. Such reference conditions also form the basis of the Swedish Environmental Quality Criteria (SEPA 2007). For acidification assessments, the contemporary pH is compared with a reference value defined by the preindustrial conditions (i.e., ΔpH = preindustrial pH – contemporary pH). Previous efforts to define the preindustrial pH have often been focused more on describing processes such as acid deposition, weathering, and the exchange and uptake of base cations, which all influence the mineral acidity. However, pH can also be strongly influenced by the organic acids in DOC. Evidence is accumulating that human activities are likely to have affected the organic acidity as well, since not only acid deposition but also land use (Guo and Gifford 2002) and climate (Worrall et al. 2004) may influence DOC.

A widespread recovery from acidification in Sweden began around 1990 (Laudon and Bishop 2002, Wright et al. 2005). At the same time, DOC concentrations began to increase in many freshwaters (Erlandsson et al. 2010). Records of DOC concentrations during the period when acidifying deposition was still increasing (i.e., pre-1975) are few and scarce; however, time series of chemical oxygen demand, a common proxy for DOC, indicate that increasing acidification was indeed accompanied by decreasing concentrations of organic acids (Erlandsson et al. 2008). If acidification has suppressed DOC, and recent DOC increases are in reality a recovery, the DOC levels observed in 2009 are likely to be closer to the preindustrial reference levels than the earlier, lower DOC values that existed when reference levels for acidification were set in national acidification assessments (when acid deposition levels in Europe and North America were much higher). Using hindcasts of acid neutralizing capacity (ANC) modeled with MAGIC (Model of Acidification of Groundwater In Catchments; Cosby et al. 2001), preindustrial reference values for pH can be calculated using two alternative reference levels for DOC: the lower "suppressed" levels observed during the height of acidification (around 1990) and the higher "recovered" levels observed two decades later.

Preindustrial reference levels for pH were calculated for the 66 lakes in the Swedish acidification monitoring program situated south of latitude 60°45' north. Most of the lakes are seasonally sampled, although for a few lakes (4 of 66), there are only winter and summer samples. The lakes can be characterized as *small* (less than two square kilometers) and *weakly buffered* (an ANC of between –20 and 370 microequivalents per liter in 2008), representative for some 12,700 acid-sensitive lakes in boreal and nemoral Sweden. The lakes differ widely in their content of organic acids; in 1990, the range in DOC concentrations was between 1.3 and 20.7 milligrams per liter (mg/L), with a median of 7.8 mg/L. In 2009, the range was between 1.4 and 31.3 mg/L, with a median of 11.6 mg/L. The median increase in DOC between 1990 and 2009 was 39%, and the increase was significant for three-quarters of the lakes.

Reference pH was calculated from ANC, aluminum, partial pressure of carbon dioxide (pCO_2), and two alternative levels for DOC, using essentially the same methodology as did Erlandsson and colleagues (2010). The chemistry in the respective endpoints was taken as the median from three years (1990–1992 for the first level and 2007–2009 for the second). Preindustrial ANC and aluminum were taken from MAGIC hindcasts, where the preindustrial period is defined as before 1857, when the water chemistry is assumed to have been in a steady state (Moldan et al. 2004), and preindustrial pCO_2 was assumed to be equal to the mean value of the observations from the two endpoints. The acid properties of DOC were modeled according to Hruška and colleagues (2003), with a model that has been tested successfully in both heavily acidified and relatively pristine areas.

With DOC levels equal to those in 1990, the range in reference pH was from 4.7 to 7.2, with a median of 6.5. With DOC levels equal to those in 2009, the range in reference pH was from 4.4 to 7.1, with a median of 6.3. The pH differences between these two alternative reference levels for DOC were only 0.2 pH units in median, but up to 1.1 units for individual lakes. The effect of changing DOC levels on reference pH is furthermore dependent on the pH interval, becoming progressively more important with declining pH below 6.5. For lakes with reference pH above 6.5 (calculated with DOC from 1990), the median difference between the two different DOC reference levels was only 0.04 units (n = 32), whereas for lakes with reference pH below 6.5, the median difference was 0.32 units (n = 34).

Even if the differences in reference pH seem small, they have a major impact on acidification assessments based on changes in pH. For example, with the lower 1990 DOC concentrations as the reference, 43% of the lakes were classified severely acidified in 1990 (ΔpH $\geq$ 0.8), whereas only 29% were classified severely acidified if the higher 2009 DOC concentrations are used as the reference (figure 1). Furthermore, by 2009, 47% of the lakes would be classified

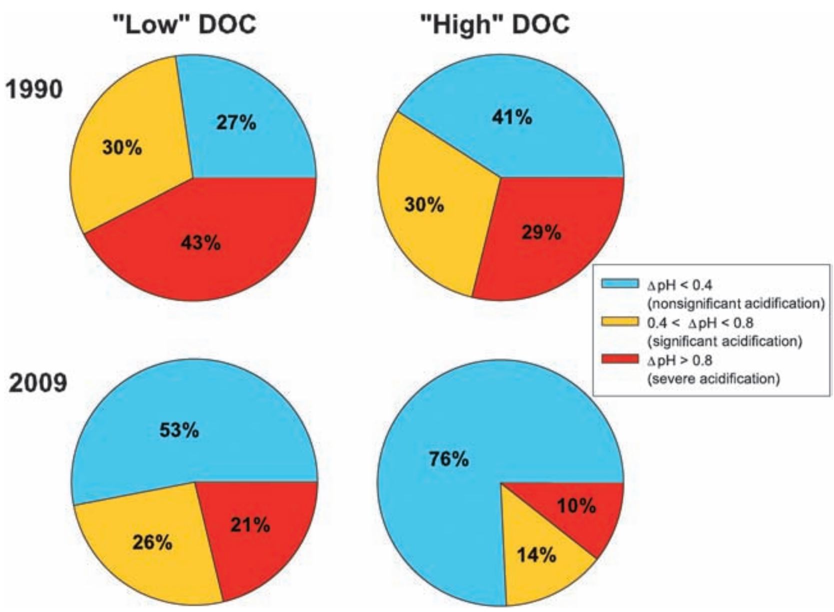

Figure 1. Acidification assessments for 1990 (upper panel) and 2008 (lower panel), according to the Swedish Environmental Quality Criteria. Assessments are based on ΔpH, the difference between contemporary and preindustrial reference pH levels. For the "low" DOC scenario, ΔpH is calculated using the DOC concentrations observed in 1990 as the preindustrial reference level; for the "high" DOC scenario, the DOC concentrations observed in 2009 are used. Lakes with ΔpH > 0.4 are defined as **significantly acidified,** *whereas lakes with ΔpH > 0.8 are defined as* **severely acidified.** *Abbreviation: DOC, dissolved organic carbon.*

as significantly acidified (ΔpH ≥ 0.4) with the lower 1990 DOC reference concentrations. With the higher 2009 DOC concentrations as the reference level for DOC, half as many lakes (24%) would be classified as significantly acidified. Considering the large number of lakes represented here, the difference between these two alternative assessments of freshwater acidification in Sweden is substantial.

It is also possible to calculate the hypothetical preindustrial DOC levels required in order for DOC suppression to fully compensate for the deposition of mineral acids—that is, implying no net change in pH between preindustrial conditions and 1990 (figure 2). It is evident that the preindustrial DOC levels would have had to have been much higher than what can be observed today in most cases, even after two decades of sustained DOC increases (18.8 mg/L in median, 75% higher than the level in 2009 for the median lake).

Policy implications

The DOC concentrations in freshwaters vary over both historical and recent time scales. At present, there is no sign that the decadal trends of increasing DOC are abating in Sweden, even though sulfate concentrations in rain and surface waters are stabilizing (Skjelkvåle et al. 2005).

The results demonstrated in this study are not intended to imply that the question of what preindustrial DOC concentrations really were has been resolved, but rather to exemplify the significance of using different DOC reference levels. To fully resolve the issue, the drivers behind the observed DOC increase must be determined. If, for example, any mechanism related to anthropogenic climate change were the main driver, the lower 1990 DOC concentrations would better represent the "unelevated" preindustrial reference levels, whereas if recovery from acidification were the main driver of the recent DOC increase, it would be more appropriate to choose the higher DOC concentrations of 2009 to represent the reference levels.

Reconstruction of historical levels of organic matter concentrations with near-infrared spectroscopy on lake sediments has yielded relatively good agreement between measured and reconstructed DOC concentrations (r^2 = .72, root mean square error of prediction = 2.6 mg/L). Application of this technique to four lakes in southern Sweden (all of them included in this study) indicates 15%–50% higher organic matter concentrations around 1850 relative to those in 2009 (Cunningham et al. 2009). For two of these lakes, the reconstructed preindustrial DOC is actually sufficiently high for DOC suppression to completely compensate for acid deposition with no net change in the pH relative to preindustrial conditions. For the other two lakes, however, much higher DOC levels than what the paleolimnological reconstructions suggest are required for full pH compensation (figure 2). This is too small a sample to draw general conclusions from, but the results do underline the importance of considering DOC reference levels in the assessment of specific water bodies.

Aside from the large effect that DOC can have on pH in weakly buffered lakes in the pH range between 5 and 6 (Köhler et al. 2001), DOC change affects freshwater ecosystems in many other ways, such as drinking-water quality, metal and organic contaminant transport and toxicity, nutrient availability, and attenuation of solar radiation (Williamson et al. 1999). Because of the concerns about further climate-related DOC increases (Worrall and Burt 2005, Jennings et al. 2010), there is a need to establish reference values for DOC in many aspects of aquatic assessment that extend far beyond the regions of weakly buffered waters where acidification can be an issue. Paleolimnological reconstructions are one approach (Rosén 2005), but this is also a challenge to the biogeochemical modeling community, which has been making recent progress in developing process-based models of DOC accounting for both soil and in-lake processes (Futter et al. 2007).

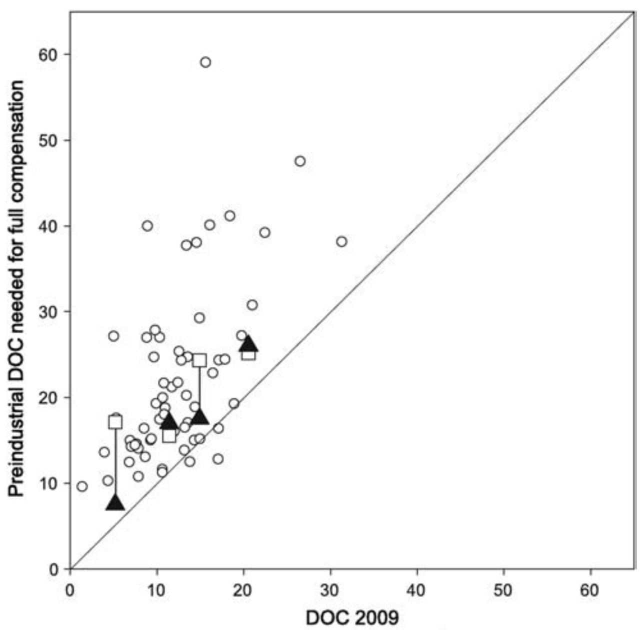

Figure 2. Hypothetical preindustrial dissolved organic carbon (DOC; in milligrams per liter) needed for full compensation of acid deposition's acidifying effects (i.e., no resulting net decline of pH between the preindustrial reference level and that in 1990). This is plotted against the DOC concentrations observed in 2009. The filled triangles represent near-infrared spectroscopy (NIRS) reconstructions of preindustrial DOC in four lakes (Cunningham et al. 2010). The open squares represent the reference DOC required for full compensation in each of those four lakes. For two of these lakes, NIRS reconstructions indicate that preindustrial DOC was sufficiently high to completely compensate for acid deposition if that acid deposition suppressed the DOC to the levels observed in those lakes in 1990.

We hope that this article has helped demonstrate how such a reference level perspective for DOC change was needed to satisfactorily address Krug and Frink's (1983) hypothesis that acid deposition merely substituted one form of acidity for another. Although it is unlikely that suppression of organic acids by anthropogenic acidifying deposition was sufficient for a one-to-one replacement of acidity, the degree of compensation is sufficient to dramatically change the assessment of acidification in southern Sweden if increases in DOC since 1990 should prove to be largely due to recovery from acidification-suppressed levels. This finding provides no reason for questioning the value of the effort made to control acid emissions, which led to wide-ranging improvements of the environment, including to human health. However, a reconsideration of the reference conditions would have major implications for the efforts to directly remediate the symptoms of acidity through liming. Remediation measures in the form of liming have been undertaken since the early 1980s in Sweden. So far, the total cost has exceeded €360 million (SEPA 2007). The decision to embark on this remediation program, and to continue it, will have been based on an inaccurate picture of the extent of acidification if acidification has been partially mitigated by suppression of DOC.

More generally, when turning to acidification as a textbook example for how environmental science can support policy, it should be remembered that the handling of natural organic acidity was a poor example of how to treat dissenting scientific views. The failure to account for organic acidity contributed to a false dichotomy between natural and anthropogenic acidification, when in fact they coexisted. The difficulty of resolving opposing viewpoints is a challenge for all policy-relevant science. Although science can indeed support the policy process, there is a peril in not seriously and respectfully considering dissenting viewpoints and alternative hypotheses with controversial policy implications. With respect to acid rain, such dissenting voices contributed to advancing the clarity of the understanding of a complex environmental issue, despite these alternative viewpoints' being eschewed by some at the time. This shortcoming in the handling of organic acidity has contributed to mistakes in Swedish remediation measures (Bishop 1997) but might be a salutary example that will help avoid mistakes with other environmental issues.

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