

Humic substances—part 7: the biogeochemistry of dissolved organic carbon and its interactions with climate change

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Abstract

Background, aim, and scope Dissolved organic matter, measured as dissolved organic carbon (DOC), is an important component of aquatic ecosystems and of the global carbon cycle. It is known that changes in DOC quality and quantity are likely to have ecological repercussions. This review has four goals: (1) to discuss potential mechanisms responsible for recent changes in aquatic DOC concentrations; (2) to provide a comprehensive overview of the interactions between DOC, nutrients, and trace metals in mainly boreal environments; (3) to explore the impact of climate change on DOC and the subsequent effects on nutrients and trace metals; and (4) to explore the potential impact of DOC cycling on climate change.

Main features We review recent research on the mechanisms responsible for recent changes in aquatic DOC concentrations, DOC interactions with trace metals, N, and P, and on the possible impacts of climate change on DOC in mainly boreal lakes. We then speculate on how climate change may affect DOC export and in-lake processing and how these changes might alter nutrient and metal export and processing. Furthermore, the potential impacts of changing DOC cycling patterns on climate change are examined.

Results It has been noted that DOC concentrations in lake and stream waters have increased during the last 30 years across much of Europe and North America. The potential reasons for this increase include increasing atmospheric CO₂ concentration, climate warming, continued N deposition, decreased sulfate deposition, and hydrological changes due to increased precipitation, droughts, and land use changes. Any change in DOC concentrations and properties in lakes and streams will also impact the acid–base chemistry of these waters and, presumably, the biological, chemical, and photochemical reactions taking place. For example, the interaction of trace metals with DOC may be significantly altered by climate change as organically complexed metals such as Cu, Fe, and Al are released during photo-oxidation of DOC. The production and loss of DOC as CO₂ from boreal lakes may also be affected by changing climate. Climate change is unlikely to be uniform spatially with some regions becoming wetter while others become drier. As a result, rates of change in DOC export and concentrations will vary regionally and the changes may be non-linear.

Discussion Climate change models predict that higher temperatures are likely to occur over most of the boreal forests in North America, Europe, and Asia over the next century. Climate change is also expected to affect the severity and frequency of storm and drought events. Two general climate scenarios emerge with which to examine possible DOC trends: warmer and wetter or warmer and drier. Increasing temperature and hydrological changes (specifically, runoff) are likely to lead to changes in the quality and quantity of DOC export from terrestrial sources to rivers and lakes as well as changes in DOC processing rates in lakes. This will alter the quality and concentrations of DOC and its constituents as well as its interactions with trace metals and the availability of nutrients. In addition,

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export rates of nutrients and metals will also change in response to changing runoff. Processing of DOC within lakes may impact climate depending on the extent to which DOC is mineralized to dissolved inorganic carbon (DIC) and evaded to the atmosphere or settles as particulate organic carbon (POC) to bottom sediments and thereby remaining in the lake. The partitioning of DOC between sediments and the atmosphere is a function of pH. Decreased DOC concentrations may also limit the burial of sulfate, as FeS, in lake sediments, thereby contributing acidity to the water by increasing the formation of H₂S. Under a warmer and drier scenario, if lake water levels fall, previously stored organic sediments may be exposed to greater aeration which would lead to greater CO₂ evasion to the atmosphere. The interaction of trace metals with DOC may be significantly altered by climate change. Iron enhances the formation of POC during irradiation of lake water with UV light and therefore may be an important pathway for transfer of allochthonous DOC to the sediments. Therefore, changing Fe/DOC ratios could affect POC formation rates. If climate change results in altered DOC chemistry (e.g., fewer and/or weaker binding sites) more trace metals could be present in their toxic and bioavailable forms. The availability of nutrients may be significantly altered by climate change. Decreased DOC concentrations in lakes may result in increased Fe colloid formation and co-incident loss of adsorbable P from the water column.

Conclusions Climate change expressed as changes in runoff and temperature will likely result in changes in aquatic DOC quality and concentration with concomitant effects on trace metals and nutrients. Changes in the quality and concentration of DOC have implications for acid–base chemistry and for the speciation and bioavailability of certain trace metals and nutrients. Moreover, changes in DOC, metals, and nutrients are likely to drive changes in rates of C evasion and storage in lake sediments.

Recommendations and perspectives The key controls on allochthonous DOC quality, quantity, and catchment export in response to climate change are still not fully understood. More detailed knowledge of these processes is required so that changes in DOC and its interactions with nutrients and trace metals can be better predicted based on changes caused by changing climate. More studies are needed concerning the effects of trace metals on DOC, the effects of changing DOC quality and quantity on trace metals and nutrients, and how runoff and temperature-related changes in DOC export affect metal and nutrient export to rivers and lakes.

Keywords Dissolved organic carbon (DOC) · Biogeochemistry · Climate change · Nutrients · Trace metals

1 Background, aim, and scope

Dissolved organic matter, measured as dissolved organic carbon (DOC), is an important component of aquatic ecosystems (see Steinberg et al. 2008) and of the global carbon cycle. As a carbon and energy source for micro-organisms in water and soil, it undergoes and is part of many important chemical and photochemical reactions and transformations. Through its constituent acids, DOC has an effect on the pH of aquatic systems, it imparts color, it attenuates both visible and UV light, thus acting as a sunscreen for aquatic micro-organisms. DOC also binds metals, affecting their toxicity and bioaccumulation, and nutrients such as N, P, Fe, Cu, and Se, thus controlling their bioavailability and mobility. Clearly, changes in DOC quality and quantity are likely to have ecological repercussions.

DOC inputs to boreal lakes are typically dominated by allochthonous sources, especially peatlands (Dillon and Molot 1997a). Water-saturated organic soils such as peat sequester relatively large amounts of organic carbon because saturation inhibits aerobic respiration. Some of the sequestered carbon is released as DIC (CO, CO₂, and CH₄) to the atmosphere and some is exported as DIC and DOC to adjacent surface waters. Annual DOC export from a catchment is highly correlated with annual runoff (Dillon and Molot 2005), hence DOC loading (sum of all inputs) to a lake is regulated in large part by local hydrology and landscape features.

The leaching of carbon from soils depends on a number of factors. DOC interactions and movement in a landscape comprise many factors (Neff and Asner 2001; Roulet and Moore 2006) so that receiving waters may exhibit a large variability in their response (e.g., CO₂ evasion rates) to climate change (Huttunen et al. 2003). Lake characteristics (e.g., size, morphometry) and hydrological and geological characteristics of the catchment also play a role (Xenopoulos et al. 2003).

Having entered a lake, DOC is gradually degraded by biological and photochemical processes (Stumm and Morgan 1996) to dissolved inorganic carbon (DIC) and particulate organic carbon (POC) (Wetzel 2001). The partitioning of DOC losses between DIC (transferred to the atmosphere) and POC (transferred to the sediments) is controlled in part by acidity which promotes photo-mineralization to DIC (Dillon and Molot 1997b; Gennings et al. 2001; Molot et al. 2005) and coagulation by releasing organically bound metals such as Al and Fe (Kopáček et al. 2006). The degradation of DOC also releases bound constituents such as P, N (Wang et al. 2000; Tarr et al. 2001; Vähätalo et al. 2003), and metals (e.g., Kopáček et al. 2005; Shiller et al. 2006; Brooks et al. 2007; Kelton et al. 2007), thereby increasing their bioavailability.

The potential mechanisms responsible for recent changes in aquatic DOC concentrations, such as increasing atmospheric CO₂ concentration, climate warming, continued N deposition, decreased sulfate deposition, and hydrological changes, are discussed in this review. Any change in DOC concentrations and properties in lakes and streams will also impact the interactions between DOC, nutrients, and trace metals.

We review how climate change may affect DOC export from terrestrial catchments to lakes and in-lake processing of DOC, and as a result, how these changes might alter nutrient and metal export and processing in lakes. We also explore the potential impact of altered in-lake DOC cycling on climate change.

2 Climate change and DOC

2.1 Recent changes in DOC concentrations

Increases in DOC concentrations in lake and stream waters during the last 30 years were reported in several studies across much of Europe and North America (Freeman et al. 2001a, 2004; Worrall et al. 2004a; Hongve et al. 2004; Evans et al. 2005; Skjelkvåle et al. 2005; Burns et al. 2006; Vuorenmaa et al. 2006). Several hypotheses have been suggested to explain these increases (discussed in more detail below) including increasing atmospheric CO₂ concentration (Freeman et al. 2004), climate warming (Freeman et al. 2001a), continued N deposition (Pregitzer et al. 2004; Findlay 2005), decreased sulfate (SO₄²⁻) deposition (Evans et al. 2006; Monteith et al. 2007), hydrological change including increased precipitation (Freeman et al. 2001a; Hejzlar et al. 2003), droughts, and altered hydrologic pathways (e.g., Hongve et al. 2004; Worrall and Burt 2008). Land use changes are also important factors influencing the transport of DOC from catchments to adjacent surface waters (Worrall et al. 2004b; Raymond and Oh 2007).

In contrast, lakes in central Ontario exhibited small and variable changes in DOC concentrations. Between 1978 and 1998, DOC loading to these lakes (loading is defined as the sum of all tributary export to a lake) did not exhibit a clear increase or decrease. Instead, loading declined during dry conditions in the middle of the study period then increased to earlier levels with loading being strongly associated with runoff patterns (Dillon and Molot 2005). These changes in loading were mirrored by smaller and variable changes in lake DOC concentrations.

2.1.1 Increasing atmospheric CO₂

Understanding the effects of elevated atmospheric CO₂ concentrations on soil organic matter accumulation and decomposition in wetland ecosystems is important for

predicting future carbon dynamics and sequestration. Although wetlands occupy a relatively small percentage of the world's land area, they store a disproportionate amount of soil C (Lavoie et al. 2005). Elevated CO₂ enhances DOC supply in peat soils and possibly into adjacent aquatic ecosystems (Kang et al. 2001). Freeman et al. (2004) observed an increase in DOC exported from peat soils under elevated CO₂ conditions which they attributed to elevated net primary productivity and increased root exudation of DOC. They suggested that the labile carbon released by roots stimulate microbial activity, leading to enhanced degradation of soil organic matter; this process is known as the 'priming mechanism' (Kuzakov 2002).

Experiments with elevated CO₂ levels significantly increased soil organic matter mineralization by 83–218% in a simulated wetland (Wolf et al. 2007). Based on natural-abundance stable carbon isotope tracing, this study showed that the increase in CO₂ production was derived from the mineralization of established soil organic matter, not recently fixed carbon compounds. Fenner et al. (2007b) proposed, however, that the proportion of DOC leachate derived from recently assimilated ¹³CO₂ was significantly increased in the enhanced CO₂ peat. They attributed the observed increase in DOC concentrations in the leachate to the switch from predominantly *Sphagnum* spp. to vascular species (namely *Juncus effusus*), leading to enhanced exudation and decomposition of the litter and peat, measured as CO₂ production. A study by Lavoie et al. (2005) gave inconclusive results for the growth of *Sphagnum* under enhanced CO₂ conditions. A consensus on these findings remains to be established.

Increased atmospheric CO₂ concentrations result in increased primary production and, consequently, increased decomposition of wetland soil organic matter, thereby resulting in increased export of DOC to streams and lakes.

2.1.2 Continuing N deposition

The documented increase of NH₃ and NO_x (NO+NO₂) emissions over the last 150 years has accelerated N deposition, compromising air and water quality and altering the functioning of terrestrial and aquatic ecosystems worldwide (Holland et al. 2005). Riverine inputs of N into the North Atlantic basin from Europe have increased by a factor of 3.5–10.6 relative to preindustrial inputs (mid-1800s). Similarly, N fluxes (from direct atmospheric deposition and runoff) into North American rivers have increased by a factor of 1.7–5.3 (Howarth et al. 1996). A possible explanation for the observed differences between Europe and North America may be due to the greater atmospheric transport of N offshore of North America, which is then deposited downwind onto the North Atlantic Ocean or Europe (Galloway et al. 1996; Prospero et al. 1996).

Concentrations of DOC in New York's Hudson River have doubled over the past 16 years. Temperature, groundwater levels, and land cover have not changed in ways that would make these viable causes for the observed increases in DOC. One plausible mechanism driving these changes is a soil microbial response to N deposition, resulting in greater export of humic material (Findlay 2005). Eight years of experimental nitrate (NO_3^-) additions to four different northern hardwood forests (Great Lakes Region of the USA) dramatically increased leaching losses of DOC (Pregitzer et al. 2004). Other recent studies also acknowledged that N deposition increases DOC and DON production (McDowell et al. 1998; Yano et al. 2000). However, other studies showed no increase in DOC production and export. Currie et al. (1996) found no significant difference in DOC concentrations in soil water from the O_a horizon after 7 years of N addition to pine and hardwood stands in the Harvard Forest, but DON concentrations and ratios of DON:DOC did increase significantly. These disparate findings indicate that other mechanisms are at least partly responsible in determining changes in soil DOC production and export.

The role of continuing N deposition on DOC export from soils is still not completely understood. Results from different field experiments do not agree on the impact of N additions to soils indicating that N deposition is not the only mechanism responsible for observed changes in soil DOC production and export.

2.1.3 Decreasing S deposition

The deposition of strong mineral acids reduces DOC concentrations in low pH (<6) irradiated water through enhanced photochemical oxidation (Gennings et al. 2001; Anesio and Granéli 2004; Molot et al. 2005). Increases in both acidity and ionic strength (associated with a high SO_4^{2-} loading) have also been shown to reduce soil solution DOC concentrations in a range of laboratory experiments with organic soils horizons (Kalbitz et al. 2000 and references therein). From this last finding, it is inferred that acid deposition may lead to lower DOC loading to lakes and lower DOC concentrations in lake waters.

On the other hand, when acid deposition is reduced DOC loading to lakes should eventually increase. Photochemical oxidation rates will also decline in step with increasing pH leading to an increase in DOC concentration in lakes. As deposition declines, mineral acidity will be partially replaced by organic acidity (Krug and Frink 1983). If declining acid deposition is having a major influence, the rise in DOC concentration may be seen as part of the recovery process in acid-sensitive waters, with “weak” organic acidity increasingly replacing “strong” mineral acidity (Skjelkvåle et al. 2005). Although an inverse

relationship has been proposed between mineral acidity and the generation of DOC (Krug and Frink 1983), Freeman et al. (2001b) observed similar proportional increases in DOC concentrations in lakes and streams (UK Acid Waters Monitoring Network) at remote, unacidified sites, as well as at those recovering from anthropogenic acidification, indicating that other mechanisms are also responsible for the observed increases in DOC concentrations.

Several recent studies suggested that changes in SO_4^{2-} , resulting from either declining deposition or water-table shifts in wetlands, could influence patterns and trends in DOC concentrations in surface waters (Clark et al. 2005, 2006; Vuorenmaa et al. 2006). Evans et al. (2006) reviewed a variety of potential drivers of increases in DOC at 22 UK streams and lakes between 1988 and 2003, and concluded that declines in SO_4^{2-} deposition and presumed improvements in soil pH (and potential decreases in soil solution ionic strength) were the most likely causes. Monteith et al. (2007) showed, through the assessment of time series data from 522 remote lakes and streams in North America and northern Europe, that rising trends in DOC concentrations between 1990 and 2004 can be explained by a simple model based solely on changes in deposition chemistry and catchment acid sensitivity. They demonstrated that DOC concentrations increased in proportion to the rates at which atmospherically deposited anthropogenic sulfur and sea salt have declined. However, Eimers et al. (2008b) provided an alternative explanation in which negative correlations between SO_4^{2-} and DOC concentrations are either directly (spring) or indirectly (summer/fall) caused by underlying relationships with hydrology.

The assessment of time series from over 500 acid-sensitive sites in North America and northern Europe showed that the tendency for DOC increases in most regions between 1990 and 2004 could be explained by changes in the acid anion concentration of atmospheric deposition (ICP Waters Report 87/2007). Increases were particularly dominant in the southernmost regions of the Nordic Countries, in the United Kingdom, and in the north-eastern U.S.; these are all areas where sulfur and/or chloride deposition have declined significantly during the 1990–2004 time period. There were strong tendencies for DOC to increase in the northern Nordic region, as well as in Ontario and Quebec, although many of these increases were not significant, suggesting that hydrology may be playing a stronger role in these regions. Atlantic Canada was the only region with little evidence of increasing DOC. For Newfoundland sites, where DOC concentrations declined, the change in SO_4^{2-} was mostly small and statistically insignificant, whereas Cl^- concentrations had increased significantly.

Although decreasing S deposition has been shown to be a major contributor to the observed increases in surface water DOC concentrations in many regions impacted by acidification, other regions, not impacted by acidification, also exhibit increases in surface water DOC concentrations. Furthermore, some acidified regions show insignificant changes in DOC concentrations in response to decreased S deposition. These disparate findings indicate that hydrology may also be an important mechanism in determining surface water DOC concentrations.

2.1.4 Increasing air temperature

Changes in temperature may directly impact DOC export from wetlands by altering DOC production via increased organic matter decomposition and mineralization which are both sensitive to variations in moisture and temperature (Dalva and Moore 1991; Christ and David 1996; Rey et al. 2005). Temperature may also affect net primary production, at least indirectly by changing the length of the growing season. Hence, changes in DOC export will depend in part on how temperature affects the difference between new production and respiration (loss), this difference being the pool that contributes to the leachable component (Schiff et al. 1997).

Increased air temperature may mean increased depth to the water table in organic soils as a result of higher evaporation rates in some regions. If the water table is lowered below the surface, the carbon sink–source relationship is likely to be disturbed because a greater percentage of the peat is available for oxidation in biochemical reactions, thereby increasing the activity of the phenol oxidase enzyme, which degrades the phenolic compounds that inhibit decomposition (Freeman et al. 2001b). Worrall and Burt (2004) associated observed increases in DOC concentrations in UK rivers with severe droughts which triggered the ‘enzymatic latch’ mechanism. The rate of peat decomposition will increase with lowered water tables, and effectively more CO₂ and DOC could be available for release. As a potential counter-balance, reduced water tables would result in a reduction in the amount of CH₄ (a relatively stronger greenhouse gas than CO₂) released because the increase in aerobic conditions will suppress the activity of the anaerobic methanogenic bacteria and decrease the volume of peat in which CH₄ oxidation may occur (Holden et al. 2007).

Pastor et al. (2003) observed reduced DOC export from experimentally warmed peat mesocosms as increased evapotranspiration led to reduced discharge, and hence, reduced DOC transport, out of the peat. These experimental findings are consistent with the observations of reduced export from forested catchments during dry conditions in central Ontario (Dillon and Molot 2005). Meyer and

Pulliam (1992) interpreted a decrease in DOC inputs to streams to soil warming that results in accelerated respiration of soil organic matter that would otherwise be transported to streams as DOC. The different possible processes responsible for the decreased DOC export to streams indicate that DOC export responses to changes in temperature and runoff will vary geographically, perhaps because peatlands in relatively wet climates like the UK do not experience the same magnitude of aeration as experienced in some parts of North America.

Any rise in temperature that accompanies elevated atmospheric CO₂ and CH₄ could also intensify aquatic respiration and emission rates (Fenner et al. 2007a). For example, increased temperature results in increased CH₄ emissions from the littoral regions of boreal lakes (Kankaala and Bergström 2004) perhaps as a result of more extensive anoxia in shallow sediments. A longer ice-free season may also lead to increased in-lake photochemical and biological consumption of allochthonous DOC, resulting in decreased DOC concentration.

Increased temperature also means a shorter frost season for soils resulting in increased export of nutrients to the lakes (Kortelainen et al. 2006) although this could be offset by decreased streamflow due to changing precipitation patterns which would exist under the warmer and drier scenario. The implications for DOC–nutrient interactions are discussed in Section 4.

Even though increased temperature results in increased decomposition of soil organic matter and production of DOC, it is the availability of water that, in part, controls DOC export. DOC export will also depend on how temperature affects the difference between new production and mineralization.

2.1.5 Change in precipitation

In the previous sections, hydrology has been invoked as a mechanism to explain disparate findings regarding the effects of continuing N deposition and changing S deposition, and air temperature on surface water DOC concentrations. In this and subsequent sections, we will examine the significance of hydrology.

The significance of hydrology on transport of DOC from terrestrial sources to the streams and then to the oceans was discussed by Tranvik and Jansson (2001) who argued that warming can affect DOC export in different ways, depending on whether it is accompanied by increased or decreased precipitation. Precipitation and discharge showed significant increasing trends in the period 1983–2000 in central Europe (Hejzlar et al. 2003). Increases in DOC concentrations and water color and changes in the concentrations of inorganic constituents (significant reduction of sulfate concentrations, but increase in acidity) in Norwegian forest

lakes during the last 20 years are well correlated with increasing amounts of precipitation, while no effect was seen with increasing temperature (Hongve et al. 2004). Raymond and Oh (2007) showed a general relationship between the discharge and precipitation in three large-scale watersheds (Mississippi, Missouri, and Ohio River, USA) and concluded that increased precipitation would result in increased DOC export. Similarly, annual DOC export and annual runoff were highly correlated in 20 forested boreal catchments in central Ontario (Dillon and Molot 2005). The substantial increase in DOC concentration in lakes and streams in Sweden during the 1970s and 1980s, despite a reduction of annual temperature (which is in contrast with Freeman et al. 2001a), was explained by the increased precipitation and runoff in these locations.

In contrast, DOC concentrations in a UK upland peatland catchment decreased with increased discharge during autumn storm events, which may be a dilution effect, but remained comparatively flow-invariant at other times of the year (Clark et al. 2007). DOC export increased during individual storm events, however, as DOC export is ultimately controlled by discharge volume, and therefore rainfall. The magnitude of change in discharge was greater than the magnitude of decline in concentrations indicating flushing of stored DOC followed by dilution (Clark et al. 2007).

The implications for long-term DOC trends therefore seem contradictory, as increased rainfall could increase export but cause an overall decrease in DOC concentrations from peatland streams. Alternatively, increased concentrations can occur due to changing DOC production and retention, but with no change in hydrology (Roulet and Moore 2006). We suspect that part of this apparent contradiction is due to the varying response of DOC export and concentrations over different time scales, e.g., short-term precipitation events (hours to days) versus melt events (days to weeks) versus annual estimates. Furthermore, numerous studies have reported long-term trends in DOC concentration; however, some studies consider changes in average measured DOC whereas others compute discharge weighted concentrations (Eimers et al. 2008c).

Eimers et al. (2008b) showed that significant increases in average DOC concentration between 1980 and 2001 at six wetland-dominated catchments (Dorset Study Area, Ontario, Canada) were driven by relatively high DOC concentrations in the latter years of record, consistent with low spring flow in these years, and were not translated into greater DOC export to downstream lakes. Such observations are not surprising since export measured downstream is a result of many interacting processes (Roulet and Moore 2006). Changes in stream flow have an important impact on trends in DOC concentration, and extrapolation of trend results from one region to another should be made

cautiously and consider methodological and reporting differences among sites.

2.1.6 Droughts

Major observed changes in DOC concentration and flux were associated with major droughts [in two UK river catchments] (Worrall and Burt 2004). Droughts are considered as a possible driver, as DOC production is thought to increase under aerated conditions, and meteorological observations have shown a change in the seasonality of precipitation in terms of drier summers and wetter winters over the last century (Worrall et al. 2004b).

Droughts could amplify DOC production by causing a drop in the water table below the long-term average position (the acrotelm–catotelm boundary, Holden and Burt 2003) triggering additional aerobic production. Evidence of the role of water table draw-down on DOC production is contradictory. Some authors have observed increased DOC concentrations in soil leachates following periods of draw-down (Tipping et al. 1999), while others have observed a reduction (Pastor et al. 2003; Watts et al. 2001; Worrall and Burt 2008) or no change (Blodau and Moore 2003) in DOC concentrations during droughts.

Several explanations have been put forward to explain the anomalous behavior in drought years: (1) lower DOC export because of reduced runoff (Pastor et al. 2003; Dillon and Molot 2005); (2) delayed/inhibited DOC release from soils because physicochemical changes in the peat structure prevent rewetting (Watts et al. 2001); (3) increased consumption of DOC as a substrate by soil microbes causing increased CO₂ efflux (Scott et al. 1998; Pastor et al. 2003; Freeman et al. 2004); and (4) reduced decomposition and production of DOC due to microbial inhibition under dry/acidic conditions (Scott et al. 1998).

Clark et al. (2005, 2006) reported that drought-related increases in SO₄²⁻ concentration at an upland blanket peat bog in the UK were associated with lower than expected DOC concentrations. They argued that declines in pH and/or increases in ionic strength caused by the episodic release of SO₄²⁻ suppressed DOC solubility in peat solution. Climate-induced drought events have been shown to have a significant influence on SO₄²⁻ export from forested catchments in central Ontario, subsequently delaying recovery of surface waters from acidification (Aherne et al. 2006) but the associated decreases in DOC export were also strongly correlated with runoff decreases (Dillon and Molot 2005). See Section 2.1.3 for related discussion.

2.1.7 Altered hydrologic pathways

Changed water pathways, due to increased total precipitation and more periods with very intensive rain, have led to more

leaching of colored and acidic organic compounds from the upper forest floor. This process has increased the color:DOC ratio and decreased the pH of lake waters (Hongve et al. 2004). Altered DOC in lake water will result in altered bulk properties of lake water including increased color and acidity (e.g., Hongve et al. 2004). In addition, we speculate that this could lead to altered cycling and bioavailability of trace metals, and perhaps altered nutrient (P, Fe, N) bioavailability.

Severe drying of soils can lead to cracking and, thus, the generation of new hydrological pathways. In soils that show hydrophobic behavior upon drying, it is possible that such flowpaths survive beyond the period of the drought that caused the initial cracking. Changes in flowpaths in peat following severe droughts has been proposed as an explanation for long-term increases in DOC concentration in streams draining peat-covered catchments across the northern hemisphere (Worrall and Burt 2008).

2.1.8 Changing land use

Land use changes influence the dynamics of DOC in soils by (1) changing the input of organic matter, (2) changing the substrate quality, and (3) altering the rates, extent, and pathways of microbial degradation and synthesis of organic matter (Cronan et al. 1992; Kalbitz et al. 2000). The soil C stocks decline after land use changes from pasture to tree plantation (i.e., tree farming), native forest to plantation, native forest to crop, and pasture to crop, while the soil C stocks increase after changes from native forest to pasture, crop to pasture, crop to plantation, and crop to secondary forest, the reverse process usually increasing soil carbon (Guo and Grifford 2002). The water quality responses to land use and management practices may be variable (Neal et al. 2005) or exhibit only a short-term impact (Kortelainen and Saukkonen, 1998) that might appear contradictory (Chantigny 2003).

Bellamy et al. (2005) used data from the National Soil Inventory of England and Wales obtained between 1978 and 2003 to show that carbon was lost at a mean rate of $0.6\% \text{ year}^{-1}$ from soils across England and Wales over the survey period. Although climate change may be partly responsible (Bellamy et al. 2005), the UK has undergone substantial land use/management changes within the same time period (Dawson and Smith 2007). Worrall et al. (2004a,b) also supposed that DOC changes driven by climate change might be accentuated by land use changes.

Land use changes could alter the relationship between precipitation and carbon export (Raymond and Oh 2007). For example, wetland loss has decreased the export of DOC to lakes and streams in parts of the USA by as much as 20–30% (Raymond et al. 2004).

3 Production and loss of CO₂ from boreal lakes

Thus far, we have reviewed how climate change may affect DOC concentrations and export, but the converse is also possible: DOC cycling may impact climate change since one of the sinks for aquatic DOC is its degradation to CO₂ and CH₄. If the balance between DOC losses to the atmosphere versus transfer to the sediments of lakes is altered, greenhouse gas production and release to the atmosphere can increase or decrease, affecting the severity of climate change. In addition, if lake water levels fall, previously protected organic sediments may be exposed to greater aeration which would lead to greater CO₂ evasion to the atmosphere (Mortsch and Quinn 1996; Kling et al. 2003; Benoy et al. 2007), but perhaps less CH₄ evasion if the sediments were initially anoxic. Since CH₄ is a more powerful greenhouse gas than CO₂, the net effect may be further temperature increases, mitigated temperature increases, or no effect at all.

It has been shown that increased precipitation is also linked to increased loss of CO₂ from large boreal lakes (Rantakari and Kortelainen 2005) which may have been due to an increase in its allochthonous DOC loading or an increase in photochemical oxidation and biological respiration rates. The link between increased precipitation and loss of CO₂ from boreal lakes is not universal, and may be related to other factors such as lake size. Smaller lakes typically have higher concentrations of and emit more CO₂, on a unit areas basis, than larger lakes (Kortelainen et al. 2006). Due to their smaller size, these lakes are able to respond more quickly to external changes and thus are probably more sensitive to climatic changes in the short term. However, Kelly et al. (2001), studying boreal lakes in northwest Ontario, smaller than the ones used by Rantakari and Kortelainen (2005), did not find a relationship between CO₂ evasion and precipitation. Instead, they found a correlation with regional weather patterns.

Loss of DOC from catchments via gas emissions from lakes is estimated to be relatively important. Dillon and Molot (1997a) estimated that 5% of net ecosystem production is returned to the atmosphere by way of emissions from lakes in central Ontario. Based on a study of Finnish lakes, Huttunen et al. (2003) concluded that carbon release from boreal lakes in general may be an important part of the overall carbon balance of the catchments because lakes cover 7–10% of the total area of Finland and Canada.

Lakes in general tend to be super-saturated with CO₂, releasing CO₂ to the atmosphere (Huttunen et al. 2003). In the case of Finnish lakes, Kortelainen et al. (2006) found that the super-saturation of CO₂ was, in part, due to respiration of organic matter in the sediment. They further found a strong correlation between CO₂ super-saturation

and O₂ under-saturation, but no correlation between CO₂ super-saturation and lake TOC concentration nor the proportion of catchment covered by wetland. These findings suggest that degradation of allochthonous DOC was not a major contributor to CO₂ super-saturation. These lakes were also sources of CH₄ during the ice-free season. In contrast, while O₂ under-saturation was correlated with CO₂ super-saturation in 33 Quebec lakes, the degree of O₂ under-saturation and net carbon flux to the atmosphere were positively correlated with DOC concentration (Prairie et al. 2002). Thus, at least in these Quebec lakes, lower DOC export would lead to a lower carbon flux to the atmosphere.

Using a global chemistry-transport model, Sanderson et al. (2006) showed that climate change will result in an increased amount of nitric acid produced and deposited to soils, acidifying them, resulting in potentially more acidified and eutrophic lakes and, as a consequence, greater CO₂ evasion from these. In Section 2.1.2, we saw how continuing N deposition may be contributing to increased DOC production in soils and possibly in increased export to streams and lakes, resulting in increased evasion from these.

4 Interaction of DOC with metals and nutrients

The above sections explored possible mechanisms influencing the export and fate of DOC in aquatic ecosystems. The potential impact of these mechanisms on DOC interactions with trace metals and nutrients is as complex as the chemistry and properties of DOC itself.

The interaction of trace metals with DOC may be significantly altered by climate change. Copper, which is most toxic in its free Cu²⁺ form, is less bioavailable when it is bound to DOC. Should climate change result in altered DOC chemistry (e.g., significantly fewer and/or weaker binding sites for Cu), the result could be more copper being present in its toxic and bioavailable Cu²⁺ form, assuming constant Cu loading. Presumably, this applies to other toxic trace metals exhibiting similar behavior with DOC. Under the scenario of decreased DOC export to lakes (Schindler et al. 1997; Dillon and Molot 2005) as well as increased photo-oxidation (due to increased UV light) of DOC, the toxicity of trace metals may increase. Brooks et al. (2007) have shown that photo-oxidation of river DOC decreases Cu–DOC complexes in most cases used in their study. The work by Shiller et al. (2006) also indicated that organically complexed metals such as Cu and Fe are released during photo-oxidation of DOC, while Kopáček et al. (2003, 2005) found it to be the case that Al and Fe were preferentially released. Unfortunately, there are no data on Cu export; however, similarly to Fe, we would expect changes in Cu export to be linked to changes in runoff and DOC export.

To the authors' knowledge, there are few studies examining how the presence of trace metals affects the chemistry of aquatic DOC. Such knowledge would allow for a better understanding of other climate change-dependent effects. Recent work by Kelton (2006) has demonstrated that iron enhances the formation of POC during irradiation of lake water with UV light and therefore may be an important pathway for transfer of allochthonous DOC to sediments. She hypothesized a physical process that excludes any conclusions regarding the chemical alteration of DOC other than removal of adsorbable fractions of DOC by settling amorphous Fe; this process has important implications for the fate of DOC in lakes. Kopáček et al. (2006) showed that not only Fe but also Al can significantly contribute to the sedimentation of POC. Increased sedimentation of DOC (in the form of POC) implies less DOC being lost from these lakes as CO₂. If there is a reduced Fe input to non-acid lakes, then reduced POC formation may result in relatively more DOC being evaded as CO₂ from these lakes or discharged downstream and a decrease in the relative amount of DOC transferred from the water column as POC to the sediment. Decreases in Fe export that were larger than decreases in DOC export under dry conditions in central Ontario (Dillon and Molot 2005) could have led to relatively lower rates of POC formation in lakes. Such activity could increase the importance of these lakes in the global C cycle as a source of CO₂, although the effects of decreased runoff on a regional scale of CO₂ fluxes must be considered.

Not only does Fe affect DOC but there is also a reverse effect whereby DOC affects the fate of Fe and, in turn, other nutrients. The rate of loss of Fe from lake water is strongly and negatively associated with DOC concentration (Molot and Dillon 2003) suggesting that DOC retards the formation of Fe colloids, which precipitate out of the water column to the sediment. Since Fe colloids have a strong affinity for P, DOC indirectly affects loss of P from the water column: decreased DOC concentrations in lakes would result in increased Fe colloid formation and coincident loss of adsorbable P from the water column. Kopáček et al. (2003, 2005) found that Al and Fe were preferentially released during photo-oxidation of DOC, which is consistent with the findings of Molot and Dillon (2003). They also suggested that the Al and Fe hydroxides formed may bind PO₄^{3−} resulting in its decreased availability. The Al and Fe hydroxides would then precipitate to the sediment, lowering the P concentration in lake water. A competing internal mechanism was reported by Komatsu et al. (2007) who predicted that increased lake water temperatures (and a longer ice-free season) will result in increased P in the water column from increased internal loading because of greater anoxia, thus leading to increased trophic conditions. However, the formation of anoxic areas

in oligotrophic lakes (the vast majority of boreal lakes are oligotrophic) is restricted to lakes that are small and sheltered.

Dillon and Evans (2001) found that there was a decrease in Fe retention (on a mass basis) over a 14-year period (1978–1992) in soft-water lakes in central Ontario, located on the Canadian Shield. It is believed that processes controlling Fe retention in these lakes probably remained unchanged during the study period, and that the lower mass retention in lakes was due to lower Fe export from their catchments under drier conditions, likely due to more oxidizing conditions in the surface of peatlands (Dillon and Molot 2005). The implications of lower Fe in boreal lakes may be reduced formation of POC, and perhaps greater DIC formation and subsequent evasion. In other words, the fate of DOC in these lakes may be altered.

Reduced DOC and Fe inputs to lake water as described by Dillon and Molot (2005) may also limit the burial of sulfate, as FeS, in lake sediments, thereby contributing acidity to the water by increasing the formation of H₂S. Increased acidity enhances the photochemical degradation of DOC (Dillon and Molot 1997b; Gennings et al. 2001; Molot et al. 2005), further decreasing its concentration, but also results in the release of organically bound metals such as Al and Fe (Kopáček et al. 2006), organically bound nutrients such as P, N, (Wang et al. 2000; Tarr et al. 2001; Vähätalo et al. 2003), and S. Regardless of the limitation of the burial of Fe as FeS, sediments of boreal lakes likely have large stores of Fe (Kortelainen et al. 2004) due to co-sedimentation of humic substances with iron oxide particles (Tipping and Woof 1983).

N and P are constituents of DOC which explains in large part why N and P export are correlated with DOC export (Dillon and Molot 1997a, 2005). Dillon and Molot (2005) speculated that permanently drier conditions with less runoff would likely lead to clearer lakes that are less productive because of reduced nutrient and DOC export. Conversely, increased runoff would lead to more colored and productive lakes.

Photochemical processes play a role in allochthonous nutrient cycling: inorganic P, nitrate plus nitrite, ammonia and amino acids are released from DOC by photo-oxidation (Wang et al. 2000; Tarr et al. 2001; Vähätalo et al. 2003) which results in increased phytoplankton production.

Increased trophic conditions (due to increased P and N) also yields increased decomposition of easily degradable organic matter, increased O₂ consumption both in the water column and sediments, and increased CO₂ evasion (Huttunen et al. 2003). Huttunen et al. (2003) have shown that CO₂ concentrations in Finnish lakes correlate positively with lake P and N concentrations. Kortelainen et al. (2006) found that CO₂ evasion from boreal lakes is related to the trophic status of the lakes. The consumption of O₂ during mineralization of

DOC may result in anaerobic conditions in the sediments and increased CH₄ emission from these (Huttunen et al. 2003). Huttunen et al. (2003) also found that while all Finnish lakes and reservoirs in their study set were net evaders of CO₂, CO₂ fluxes were higher from lakes and reservoirs with peatlands or managed forests in their catchment area and from eutrophic lakes.

5 Impact of changing DOC on lake water chemistry

Any change in DOC concentrations and properties in lakes and streams will also impact the acid–base chemistry of these waters and, presumably, the chemical and photochemical reactions taking place and the production of CO₂. Hongve et al. (2004) observed an increased color: DOC ratio and a decreased pH of lake waters due to altered hydrologic pathways resulting from climate change. They speculate that the different color of the water is an indication of changing DOC quality. Molot et al. (2005) also noted that pH affects photochemical DOC loss and photobleaching rates differently, hence climate mediated changes in lake pH are likely to affect water clarity even where DOC concentration remains unchanged.

Bertilsson and Tranvik (2000) suggest that although there is a large variability in water chemistry from lake to lake, photoproducts such as DIC and low molecular weight acids are universally produced in lake water exposed to sunlight. They further speculate that the variability in DIC production rates in lakes (after normalizing for absorbed radiation energy) could partly be attributed to general water chemistry parameters such as pH, iron concentration, and conductivity. There is no evidence currently available to indicate whether end products other than the amount of DIC and the type of low molecular weight acids produced will differ as a result of climate change, but we can speculate that the rate at which DOC is degraded will be altered, because DOC degradation rates are temperature-dependent (Cabaniss et al. 2005). A comprehensive review of the interactive effects of ozone depletion and climate change on biogeochemical cycles was presented by Zepp et al. (2003).

6 Future climate trends and their effect on DOC cycling

While climate change models predict that higher temperatures are likely to occur throughout most of the boreal forest regions in North America, Europe and Asia over the next century, model predictions of regional changes in precipitation, evapotranspiration and, hence, runoff are much more uncertain (see review by Lavoie et al. 2005). Models also suggest that climate change is unlikely to be

uniform spatially. Some regions may become wetter while others become drier. Climate change is also expected to change the severity and frequency of storm and drought events, change seasonal runoff patterns, and increase the length of the ice-free season. Rates of change in DOC export and concentrations will thus vary regionally and the changes may be non-linear (e.g., ICP Waters Report 87/2007; Eimers et al. 2008a). The effects of changing temperature and precipitation will be compounded by continued elevated N and decreasing S deposition.

Climate change models predict that higher temperatures are likely to occur over most of the boreal forest regions in North America, Europe and Asia over the next century. While it is difficult to predict regional climate trends and, thus, future regional trends in DOC export and concentrations, two general climate scenarios emerge with which to examine possible DOC trends: warmer and wetter and warmer and drier. We also need to consider a scenario with warmer temperatures but no change in runoff. Whatever the future brings, increasing temperature and hydrological changes are likely to lead to changes in DOC export and DOC processing rates in lakes which will alter concentrations of DOC and its constituents.

6.1 Warmer and constant runoff scenario

A scenario with a warmer climate with runoff remaining constant may lead to further increases in DOC concentrations, with complex consequences for surface waters including increased organic acidity, increased buffering of changes in pH, increased water coloration, and decreased visible light and UV-B penetration within the water column (Skjelkvåle et al. 2005). Alternatively, this scenario may *not* lead to further increases in DOC concentrations, depending on the net difference between soil production and respiration rates, especially in wetlands (see section 2.1.4). Increasing DOC concentrations in boreal soil water would have a significant negative impact on soil recovery from acidification, with elevated organic acidity lowering soil water pH by severely depleting soil base saturation (Evans 2005).

6.2 Warmer and wetter scenario

Several studies have shown that increased precipitation and runoff lead to increased DOC export and concentrations regardless of temperature changes (Worrall and Burt 2004; Dillon and Molot 2005). A warmer and wetter climate and increased concentrations of atmospheric CO₂ can increase primary productivity (Freeman et al. 2004), leading to more plant material in the soil being available for microbial production of DOC. Increased leaching may lead to higher surface water DOC concentrations (Hongve et al. 2004).

6.3 Warmer and drier scenario

On the other hand, if temperatures increase in conjunction with decreased runoff then increased DOC export and concentrations may not materialize and may, in fact, decrease (Schindler et al. 1997; Dillon and Molot 2005). Warmer and drier conditions generally resulted in decreased inputs of silica, DOC, base cations, and phosphorus from streams to the lakes in the Experimental Lake Area (Schindler et al. 1996).

7 Conclusions

There are several potential mechanisms responsible for recent changes in aquatic DOC concentrations, including increasing atmospheric CO₂ concentration, climate warming, continued N deposition, decreased sulfate deposition, and hydrological changes.

Climate change appears to be a significant driver of observed changes in aquatic DOC concentrations. Climate change models predict that higher temperatures are likely to occur over most of the boreal forests in North America, Europe and Asia over the next century. Two general climate scenarios emerge, namely warmer and wetter or warmer and drier. Climate change expressed via changes in runoff and temperature will likely result in changes in aquatic DOC concentrations with concomitant effects on trace metals and nutrients.

Changes in the quality and concentration of aquatic DOC have implications for lake acid–base chemistry and for the speciation and bioavailability of certain trace metals and nutrients. The interaction of trace metals with DOC may be significantly altered by climate change as organically complexed metals such as Cu, Fe, and Al are released during photo-oxidation of DOC. If climate change results in altered DOC chemistry (e.g., fewer and/or weaker binding sites), more trace metals could be present in their toxic and bioavailable forms.

Moreover, changes in DOC, metals and nutrients are likely to drive changes in rates of C evasion and storage in lake sediments, as the partitioning of DOC to POC (goes to sediment) and DIC (evaded as CO₂) is altered. However, the key controls (runoff, temperature, soil chemistry) on allochthonous DOC quality and catchment export are still not fully understood. Furthermore, the partitioning of DOC between lake sediments and the atmosphere is a function of pH.

Predicted future climate scenarios include a warmer and drier scenario where, if lake water levels fall, previously stored organic sediments may be exposed to greater aeration, which would lead to greater CO₂ evasion to the atmosphere. Under a warmer and wetter scenario, long-term

DOC trends seem contradictory, as increased rainfall could increase export but cause an overall decrease in DOC concentrations from peatland streams to lakes. Alternatively, increased concentrations can occur due to changing DOC production and retention, but with no change in hydrology. Part of this apparent contradiction is due to the varying response of DOC export and concentrations over different time scales as well as how DOC changes are measured, whether changes in average measured DOC or discharge weighted DOC concentrations.

Contradictory findings reported herein suggest that descriptive (e.g., correlative) studies have their limitations and that detailed modeling studies that integrate key controls are needed to allow testing of various scenarios. Similarly, more studies are also needed to explore how runoff and temperature-related changes in DOC export affect metal and nutrient export to rivers and lakes. Models are typically developed using results from small areas, hence, attention needs to be paid to scaling up the models to much larger regional scales.

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