Durham University

Insights

Institute of Advanced Study

Water Colour: Processes Affecting Riverine Organic Carbon Concentration

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Volume 3 2010 Number 8

ISSN 1756-2074

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WATER COLOUR: PROCESSES AFFECTING RIVERINE ORGANIC CARBON CONCENTRATION

Several recent studies have observed increasing trends in aquatic dissolved organic carbon (DOC), and several hypotheses have been reported that mainly focus on changes in climate, land cover and acid deposition. Here I outline further processes that can be hypothesised to affect aquatic DOC significantly, in particular regional variations in photodegradation, transfer of carbon between dissolved, colloidal and particulate forms, and the dehydration and freezing of organic matter.

The composition, concentration and flux of dissolved organic carbon (DOC) play key roles in the biogeochemistry of aquatic systems. In the northern hemisphere temperate region, increases in aquatic DOC concentrations have been recorded over the last two decades (Hejzlar et al., 2003; Findlay, 2005; Skjelkvale et al., 2005; Worrall et al., 2005; Burns et al., 2006). In particular, a number of recent studies have highlighted carbon losses from soils and increasing DOC concentrations and export in UK surface waters, particularly associated with increases in water colour, predominantly in peat rich catchments (Bellamy et al., 2005; Freeman et al., 2001; Worrall et al., 2003; 2005). Many processes have been invoked to explain these DOC trends, including changes in land cover, temperature, drought (and associated wetland water table), acidification and river flow. Evans et al. (2006) demonstrated an inverse relationship between increasing DOC concentrations in UK surface waters and declining sulphur deposition since the 1980s. Monteith et al. (2007) conclude from a study of European and North American rivers that changing atmospheric deposition (sulphate from pollution and chloride from sea spray) appear to be the most likely mechanisms to explain increasing aquatic DOC in relatively pristine catchments.

In contrast, some major rivers have shown a clear decrease in DOC over time: within the Yukon River basin this has been suggested to be due to increased flow path, residence time and microbial mineralisation of DOC in the soil active layer and groundwater (Striegl et al., 2005). It seems that increasing temperatures from global climate change could therefore result in decreasing DOC export from this, and other, permafrost affected systems. Clearly the changes in aquatic DOC reported in a number of northern hemisphere catchments are not due to a single factor but a combination of processes resulting from potential changes in land use, post industrial clean-up in emissions and through global climate change. Here I highlight a number of other potential environmental variables which may also contribute to the observed aquatic DOC variations in some northern hemisphere catchments.

Environmental factors that are known, or can be hypothesised, to affect aquatic DOC concentration are:

(1) Changes in atmospheric chemistry, which changes atmospheric aerosol concentration.
(2) Factors associated with climate change, which affect soil productivity, degradation and mobilisation within a catchment.
(3) Soil and land cover characteristics.

Of these, catchment soil characteristics and their effect on DOC production, degradation and transport are relatively well understood (Marschner and Kalbitz, 2003). The impact of changes in atmospheric chemistry through sulphate and sea salt deposition and its effect on DOC mobilisation have also been thoroughly investigated (Evans et al., 2006; Monteith et al., 2007), although nitrate deposition on soil DOC has effects which are relatively poorly understood (Waldrop and Zak., 2006) yet which have been evoked to try to explain aquatic DOC trends (Findlay, 2005; Worrall et al., 2006).

Photochemical and microbial impacts on dissolved organic matter (DOM) are well known (Mopper and Kieber, 2002; Moran and Covert, 2003; Cory et al., 2007). Terrestrial DOM is often highly susceptible to photochemical breakdown; DOM derived from both an Arctic tundra lake and a tropic river have been shown to be highly photochemically reactive (Amon and Meon, 2004; Spencer et al., 2009) and photochemical degradation has been shown to produce a suite of biologically labile photoproducts (Moran and Covert, 2003). Changes in irradiance in surface waters will also result in increasing photodissolution, resulting in the transfer of some particulate organic matter (POM) into the dissolved phase (Mayer et al., 2006).

Resuspension of sediments that have absorbed organic matter is another potential source of elevated DOC, particularly if it brings DOC to within the photic zone where it can be photodegraded. Kieber et al. (2006) demonstrate that the combination of sediment resuspension and DOC photodegradation can produce the same order of magnitude of DOC as present within the river. Although most likely to be important in estuaries where resuspension of sediment is more likely, this process might also be invoked in rivers dominated by fine grained sediments, and may change in importance under future climate change scenarios that predict significant changes in precipitation and river discharge. Finally, a regional reduction in irradiance caused by increases in anthropogenic aerosols during industrialisation (Stanhill and Cohen, 2005) may have regional affects on DOC photodegradation. The amount of ‘dimming’ has historically been spatially highly variable, with maximum dimming coincident with the zone of highest population and industrialisation.

Two processes which have been demonstrated to have significant effects on soil DOC and yet have received little attention within aquatic DOC budgets are the effects of freezing and dehydration. Both have environmental relevance, particularly under future climate scenarios, where one might observe a changed frequency of freezing events with warmer temperatures, and increased dehydration events in drier summers and/or increased hydration in wetter winters. Hydration/dehydration has been shown to change the structure and fractal dimensions of humic substance aggregates (Redwood et al., 2005) and the conformation, volume and hydrophobicity of marine sedimentary organic matter (Liu and Lee, 2006). Hydration and dehydration are important environmental processes, e.g. in the drying of soil derived DOC and of DOC within rivers and lakes due to drought and abstraction, which significantly change DOC structure in the environment. Little data is available to quantify the change in aquatic DOC with dehydration (for an exception see Hudson et al., 2009), but soil extracted carbon has been shown to increase in DOC by 420–470% with air drying (Kaiser et al., 2001), with an increase in DOC of hydrophilic character indicative of a disrupted microbial biomass source. These increases in DOC are greater than those predicted from temperature effects on soil microbial activity and CO_2 production, which have lead to Q_{10} values (the increase in DOC with a 10°C temperature increase) of between x1.33 to 3.66 (Freeman et al., 2001; Evans et al., 2006).

Limited data is also available on the effects of freezing DOC. Experimental results on the effects of freezing of upland coloured river waters (Spencer et al., 2007) show that a single freeze-thaw cycle on DOC has a small and variable decrease in DOC (3.2 ± 5.2%) depending on its source, with the DOC aggregating to form particulate organic carbon (POC) after thawing. Equivalent experimentation on soil extracted DOC showed an increase in DOC upon freezing (+99–142%), hypothesised again to be due to the disruption of microbially derived material. Freezing of soil DOC could potentially affect aquatic DOC to a greater extent than factors such as temperature or sulphate deposition.

There is a large variability and uncertainty in both the magnitude and direction of possible changes in aquatic DOC. Combined with the fact that different processes act on regional or hemispheric scale (e.g. temperature, optical dimming, atmospheric CO_2), local or catchment specific scale (precipitation, soil characteristics, land use), or both (e.g. sulphate and nitrate deposition), it is clear that simple correlations between aquatic DOC trends and any one process will be rarely observed. Furthermore, aquatic DOC is just a fraction of the total organic matter present in freshwater systems that represents an important form of energy fuelling stream ecosystems (Webster and Meyer, 1997; Battin et al., 2008) and which provides useful biogeochemical functions (Thacker et al., 2005; Buffle, 2006). Indeed, the focus on DOC has ignored increases in inorganic carbon observed in rivers due to urbanisation (Baker et al., 2008). Highlighted are several processes where organic matter moves from the operationally defined ‘dissolved’ fraction to larger size fractions (e.g. freezing), and vice versa (e.g. photodegradation), suggesting that future research may benefit from the measurement and characterisation of all size fractions (dissolved, colloidal, particulate) to put any trends in the dissolved fraction into context. Substantial experimental work, combined with process modelling, will be required if future trends in both dissolved and total organic carbon concentration and flux are to be predicted.

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