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Contemporary changes in dissolved organic carbon (DOC) in human-dominated rivers: is there a role for DOC management?

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SUMMARY

1. Dissolved organic carbon (DOC) plays a central role in the dynamics of stream and river ecosystems, affecting processes such as metabolism, the balance between autotrophy and heterotrophy, acidity, nutrient uptake and bioavailability of toxic compounds. However, despite its importance to stream processes, restoration and management activities rarely incorporate DOC as a major management criterion.
2. Lotic DOC pools reflect terrestrial organic carbon accumulation, transfer to the river channel and aquatic processing. In pristine landscapes, characteristics such as topography, climate, and landscape composition are strong predictors of terrestrial accumulation and transfer. Within aquatic systems, the quantity and form of DOC are altered by a variety of processes including primary production, microbial breakdown, sorption to particles and photodegradation.
3. Terrestrial accumulation, transfer and aquatic processing of DOC in agricultural and other human-dominated landscapes are all subject to substantial change. Consequently, DOC pools in agricultural streams likely differ from historic conditions and now include more labile material and low concentrations of a variety of ubiquitous synthetic organic compounds (e.g. pesticides, antibiotics).
4. Although DOC change in agricultural streams and associated ecological consequences are expected to be widespread, current understanding and relevant data needed to manage affected systems are surprisingly scarce.
5. Wetland and riparian restoration projects have variable effects on fluvial DOC regimes, but management at this intermediate scale is a realistic compromise between the small extent of most restoration projects and the large spatial scale over which organic carbon impairment occurs.

Keywords: agriculture, dissolved organic carbon, land-use change, restoration, riparian

Introduction

Improving and protecting water quality, both for human needs and to sustain aquatic ecosystems, has emerged as a major global challenge in the 20th and 21st centuries. The Clean Water Act in the United States and the European Union's Water Framework Directive are examples of legislation intended to ensure the long-term sustainability of water quality and aquatic ecosystems. Despite these initiatives, progress towards these goals has been limited. In the U.S. alone, 44% of rivers are considered impaired

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and in need of some form of water quality management (EPA, 2004).

Water quality impairment is a multivariate problem, with multiple causes and consequences (Ormerod *et al.*, 2010). Yet, management and restoration efforts often focus on one or a few variables from a limited set that typically includes nitrogen, phosphorus, sediment, habitat structure or flow. Changing the load or concentration of organic carbon (OC) in streams and rivers rarely motivates management activities. Exceptions include policies and activities intended to reduce organic matter loading from sewage effluents, prevent manure (organic fertilizer) inputs during periods of intense runoff, increase carbon sequestration or minimise costs associated with dissolved organic carbon (DOC) removal from drinking water sources. Notably, only two of these cases (point source control, preventing manure spills) involve a goal of improved stream 'health' or 'integrity'. Thus, for management activities that intend to improve or maintain stream status, carbon at best takes a back seat to other priorities.

Carbon's low profile in the context of stream impairment and management belies the prominent role of carbon cycling in determining ecosystem structure and function in streams and lakes. Prairie (2008) eloquently made the point that OC plays a slightly different role than nutrients in aquatic systems, referring to it as 'the great modulator' – that is, OC modifies the influence and consequence of other chemicals and processes in lakes and rivers. For example, in addition to its well-known role as an energy source for heterotrophs, OC influences light and temperature regimes by absorbing incoming solar radiation, affects transport and bioavailability of heavy metals and controls pH in many low-alkalinity fresh waters. As such, understanding how human activities alter natural OC regimes and the ecological consequences of these changes in streams and rivers in human-dominated landscapes needs to be part of an overall approach to the long-term management and sustainability of these environments.

Our overarching objectives for this study are to review how human land use influences both the quantity and quality of OC in streams and rivers and to consider the potential for management and restoration activities to ameliorate anthropogenic modifications to fluvial OC regimes. We focus primarily on DOC because it is the major OC pool in most aquatic ecosystems (Wetzel, 2001) and on agriculture because it is the most widespread cause of water quality impairment (EPA, 2004; MEA, 2005). We consider these objectives by addressing three specific questions: (i) how do human land-use activities affect the quantity and quality of DOC in streams and rivers? (ii) what are possible consequences of human modifications to fluvial DOC regimes? and (iii) what management activities might help minimise changes to a system's natural DOC regime? Answers to these questions are not singular and often not known. Thus, our approach is to highlight the variety of changes that result from human activities as well as knowledge gaps that need to be addressed to improve our understanding and management of lotic ecosystems.

How do human activities affect the quantity and quality of DOC in streams and rivers?

The base case

Because of the central significance of DOC to aquatic ecosystems, and indeed, to all ecosystems, several synthesis papers have examined carbon export from land to water and in-channel dynamics (e.g. Hope, Billet & Cresser, 1994; Mulholland, 1997; Findlay & Sinsabaugh, 1999; Sobek *et al.*, 2007; Battin *et al.*, 2008; Tank *et al.*, 2010a). Almost without exception, these papers acknowledge the likelihood of strong human influences on OC dynamics in streams and rivers and emphasise the need to better understand these effects. But there is little subsequent coverage of the topic, in large part because consideration of human influences on OC has been a relatively recent pursuit. We begin by summarizing patterns and controls on DOC that emerge from these synthesis papers. Despite differences in sites, temporal resolution or metrics used, there is substantial agreement regarding the drivers of DOC in streams and rivers. We refer to this consensus view as the 'base case' and use it as a starting point for considering how human activities influence lotic DOC dynamics.

The controls on stream and river DOC can be viewed as a function of terrestrial accumulation, transfer to the channel and in-stream processing (Fig. 1). Perhaps with the exception of open-canopy streams, lotic DOC is dominated by terrestrial sources (Aitkenhead-Peterson, McDowell & Neff, 2003; Bertilsson & Jones, 2003), so accumulation of organic

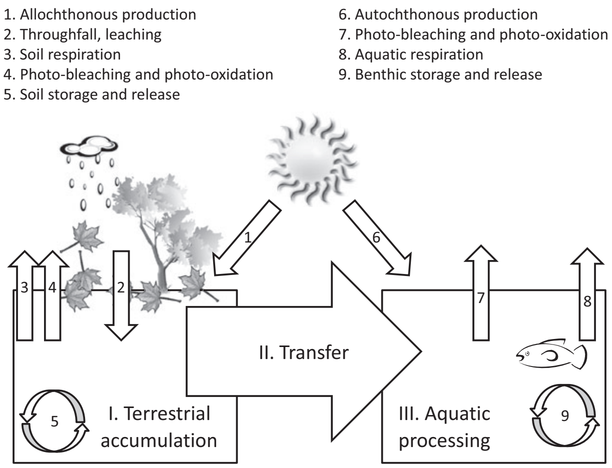

Fig. 1 Terrestrial accumulation, transfer and aquatic processing of lotic dissolved organic carbon under natural conditions (the base case). Soil/benthic storage and release includes sorption of dissolved organic carbon to particles, and release through leaching of particulate organic matter. Sorbed dissolved organic carbon may be respired or released by desorption. Both particulate and dissolved organic carbon may be transferred from terrestrial to aquatic systems.

matter in the soil environment sets the first constraint on aquatic DOC. The next determinant is the capacity to move OC from terrestrial sources to the channel. Transfer is largely hydrologic, although atmospheric inputs (especially from streamside vegetation) can make important seasonal contributions and dominate particulate OC (POC) inputs (Webster & Meyer, 1997). In-stream leaching of terrestrial POC and gross primary production add DOC, although this latter source is often minor compared to terrestrial loading. Finally, in-stream processing by photooxidation and microbial respiration transform and remove DOC. Collectively, this formula of source, transfer and processing dictates both the quantity and quality of stream DOC loads.

The next step in examining stream DOC regimes is to consider the relative influence of the three base case processes. The major roles of terrestrial accumulation and hydrologic delivery on stream DOC are underscored by a wealth of studies relating landscape and climate attributes to aquatic concentrations or loads. Land cover provides a strong predictor of terrestrial accumulation, while climate variables are typically indicators of hydrologic connection between uplands and the channel. Such investigations have met with good success at local (e.g. Frost *et al.*, 2006; Ågren *et al.*, 2007), regional (e.g. Gorham *et al.*, 1998; Gergel, Turner & Kratz, 1999) and continental to global scales (Mulholland, 1997; Aitkenhead-Peterson & McDowell, 2000), routinely explaining 50–80% of observed variance in DOC among sites. Predictors that frequently appear in such statistical models include wetland cover, topography, precipitation and soil type (reviewed by Hope *et al.*, 1994; Mulholland, 2003), all of which can be related to the basic processes of terrestrial OC accumulation and transfer to the channel.

Once terrestrial DOC is delivered to the aquatic environment, its quantity and quality can be modified by microbial processing, respiration, sedimentation, adsorption/desorption, photobleaching and photooxidation. POC leaching and *in situ* primary production contribute new DOC, and the latter source differs from terrestrial material in its susceptibility to microbial and photochemical actions. The role of aquatic processing in changing the composition and size of the DOC pool has been a topic of growing interest and debate, with several lines of evidence indicating that the fraction of DOC subject to degradation is usually relatively small (<5–30%). Additionally, much of the biologically available pool is derived from aquatic algal primary production rather than terrigenous sources (e.g. Cole, Likens & Strayer, 1982; del Giorgio & Davis, 2003). More recalcitrant fractions are transported long distances (kilometres) before they are retained or mineralised by biological or physical processes (Worrall, Burt & Adamson, 2006; Kaplan *et al.*, 2008). Thus, the two key constraints on the magnitude of aquatic processing are the overall lability of the DOC pool, and the time available for uptake or transformation of this material – that is, water residence time (Schindler *et al.*, 1992). Given the recalcitrant nature of most DOC in streams (Thurman, 1985) and characteristically brief water residence times of fluvial systems, long DOC transport distances are likely to be the base case norm.

Effects of human land use

Human activities have a range of consequences on streams and catchments, but routinely involve changes in plant cover, catchment hydrology, soil attributes and nutrient inputs, especially in agricultural areas (Allan, 2004; Millenium Ecosystem Assessment [MEA], 2005). Agricultural extent and crop selection represent strong forcings on river DOC quantity and lability. From a global assessment based on data from 1992 (Leff, Ramankutty & Foley, 2004), major crop types ranked in order of decreasing coverage were wheat, maize, rice, barley, soybeans, pulses and cotton (Table 1). C : N ratios vary widely among these crop types, and in many cases, ratios are noticeably lower or higher than for native vegetation. Other basic differences in organic composition include the amount and form of lignins and tannins (Kögel-Knabner, 2002) and overall chemical diversity of crop sources relative to species-rich native plant communities. These are obvious and well-known contrasts in the material that is the primary input to the soil carbon pool, and then eventually, the aquatic pool.

Given the basic formula of terrestrial accumulation, hydrologic delivery to the channel and aquatic processing, it is reasonable to assume that human land uses strongly affect DOC loads in streams. Yet, while some studies have been able to detect a clear signal of land use on stream DOC, others have not. Agriculture (and other human land uses) has been associated with increased, decreased and undetectable changes in DOC (Table 2). As will be discussed below, these mixed responses are perhaps not surprising given the diversity of farming practices (and other land uses) and their affiliated effects on terrestrial and aquatic carbon cycling.

While the direction and magnitude of the agricultural signal on fluvial DOC may be ambiguous, divergence in the composition of the DOC pool between undisturbed and human-impacted catchments is emerging as a consistent observation across disparate locations and land uses. Changes include shifts from high- to low-molecular-weight DOC, increased redox state, reduced aromaticity and in general, increased lability. These differences have been attributed to altered terrestrial sources as well as greater *in situ* DOC production (Cronan, Piampiano & Patterson, 1999; Wilson & Xenopoulos, 2008; Petrone, Richards & Grierson, 2009).

In the following section, we return to the accumulation-transfer-processing framework to consider how human land use – particularly agricultural activities – affects terrestrial pools of OC (accumulation), the connections between land and water (transfer), and the production and fate of DOC in streams and rivers (processing) (Fig. 2). The intent of this overview is to highlight the range of changes that can influence DOC quantity and quality, in either opposing or reinforcing directions.

Table 1 1992 global crop coverages (Leff *et al.* 2004) and representative mean values (±1 SD) for atomic carbon to nitrogen (C : N) ratios for residues of major world crops and for natural vegetation types

Plant type	Coverage (1000 km^2)	C : N ratio	Citation
Crops			
Wheat	4028	51–120	Nicolardot *et al.* (2001)
Maize	2271	62–150	Ilukor & Oluka (1995) and Nicolardot *et al.* (2001)
Rice	1956	49–62	Toma & Hatano (2007) and Liu *et al.* (2009)
Barley	1580	68–84	Ambus *et al.* (2001) and Müller *et al.* (2003)
Soybeans	927	14–16	Ilukor & Oluka (1995) and Toma & Hatano (2007)
Pulses*	794	10–16	Rannells & Wagger (1997) and Hood *et al.* (2000)
Cotton	534	18–29	Ilukor & Oluka (1995) and Muhammad *et al.* (2011)
Potatoes	501	29.7 ± 6.4	Ilukor & Oluka (1995)
Sugarcane (husks)	265	99–142	Ilukor & Oluka (1995) and Muhammad *et al.* (2011)
Natural vegetation			
Terrestrial autotrophs		36 ± 23	Elser *et al.* (2000)
Temperate broad leaf (leaves)		25	Vitousek *et al.* (1988)
Sub-alpine conifer (needles)		49	Vitousek *et al.* (1988)
Tropical/sub-tropical (leaves)		22–33	Vitousek *et al.* (1988)
C3 grasses		35–45	Murphy *et al.* (2002)
C4 grasses		50–90	Murphy *et al.* (2002)
Sphagnum moss		68–95	Bragazza *et al.* (2010)
Freshwater macrophytes		17–21	Duarte (1992) and Demars & Edwards (2008)

*Beans, peas, lentils, vetch, lupines.

Table 2 Representative examples of studies examining effects of land use on dissolved organic carbon (DOC) concentration or flux in streams and rivers

Land cover	Land coverage variable	Response variable	Direction of change	Region	Citation
Agriculture	Per cent agriculture in catchment	Conc	Positive	Western US	Chow *et al.* (2007)
	Per cent agriculture in catchment	Conc	Positive	Northeastern US	Chen & Driscoll (2009)
	Per cent agriculture in catchment	Conc	Negative	Northeastern US	Cronan *et al.* (1999)
	Per cent agriculture in catchment	Load	None	Scotland	Aitkenhead-Peterson *et al.* (2007)
	Per cent pasture in catchment	Conc	Positive	Southeastern US	Molinero & Burke (2009)
	Manure inputs	Conc	Positive		
	Buffer strip presence and type	Load	None	Central US	Veum *et al.* (2009)
Forestry	Clear-cutting	Conc	Negative	Southeastern US	Meyer & Tate (1983)
		Load	Negative		
	Presence of clear-cut sections	Conc	Positive	Northern Sweden	Laudon *et al.* (2009)
	Extent of forest harvest	Conc	None	Southeastern US	Knoepp & Clinton (2009)
Urban	Per cent road coverage in catchment	Conc	Negative	Southeastern US	Maloney *et al.* (2005)
	Per cent urban coverage in catchment	Conc	Positive	Southern US	Aitkenhead-Peterson *et al.* (2009)

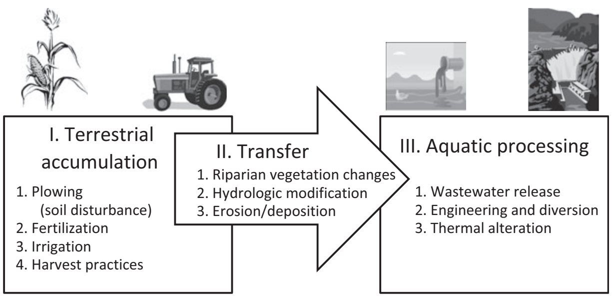

Fig. 2 Major categories of anthropogenic influence on lotic dissolved organic carbon. Plowing and other forms of soil disturbance such as planting or animal stocking disrupt soil structure, increase susceptibility to erosion and influence turnover of soil organic carbon pools. Harvest practices include factors such as crop selection in farm lands or tree type in silviculture, and timing and method of harvest for crops or timber. Hydrologic modification includes changes in surface-groundwater connectivity and the timing and magnitude of runoff resulting from attributes such as extent of impervious cover, drainage ditches or soil disturbance in the basin or riparian zone. Engineering and diversion includes factors such as the density and size of dams and reservoirs, and characteristics of flood control or water supply infrastructure.

Terrestrial accumulation

The base case highlights the significance of terrestrial OC stocks on stream DOC, and it is clear that human activities have substantial effects on terrestrial carbon pools. Agriculture, especially cropping, is associated with reduced terrestrial OC storage (Ogle, Breidt & Paustian, 2005; McLauchlan, 2006), so it is reasonable to hypothesise that soil OC (SOC) losses should have clear consequences for aquatic DOC (Sickman *et al.*, 2010). Yet, investigating the aquatic consequences of this seemingly simple, directional change in terrestrial OC highlights a diverse array of processes that may cause increases, decreases or no net change in stream OC loads in agricultural areas.

Converting natural lands to row crop agriculture causes substantial loss of OC stored in soils because of increased erosion and decomposition rates associated with physical disruption and aeration by tilling or lowering of the water table (Guo & Gifford, 2002; Jarecki & Lal, 2003). In the U.S., much of the best and most productive agricultural land occurs in low-lying, low-relief regions that were once dominated by prairies and wetlands habitats that are characterised by substantial below-ground carbon stocks (Smith & Johnson, 2003; Bridgham *et al.*, 2006). For example, Ohio, Indiana, Illinois, Iowa and Missouri have lost over 85% of their historic wetlands (Dahl, 1990) and 85–99% of the native prairie (Sampson & Knopf, 1994) due predominantly to agricultural conversion. Similarly, vast peatland areas were drained to increase farming and forestry production in the U.K. and elsewhere in northern Europe, causing substantial C losses from these environments (Holden, Chapman & Labadz, 2004; Armstrong *et al.*, 2010).

SOC losses following agricultural conversion often continue for decades (McLauchlan, 2006), but the period of initial mobilization of DOC from mineral soil appears to be shorter, lasting anywhere from <2 to 10 years (Chantigny, 2003). Further, at least some of the eroded SOC may be redistributed and buried in other terrestrial locations, never reaching the aquatic environment (Van Oost *et al.*, 2007). Nonetheless, the net long-term effect of agricultural conversion is a smaller terrestrial OC pool relative to native conditions, meaning that the potential supply of OC available for aquatic loading is reduced. Thus, it is often assumed that the historic loss of wetlands and SOC has resulted in lower contemporary DOC loads and concentrations in many agricultural streams (e.g. Royer & David, 2005; Dalzell, Filley & Harbor, 2007).

Declines in SOC pools associated with land conversion are accompanied by other agricultural practices that can complicate land use-stream DOC relationships. Modern changes in farming practices such as reduced plowing depth or no-till agriculture have been adopted to slow or even reverse soil and SOC losses (Smith, 2004; Ogle *et al.*, 2005). Amendments of crop residues, organic fertilizers and manure disposal also add to the SOC pool. Because these additions are not fully integrated into the soil structure, they may be easily mobilized and cause both short-term and more sustained increases in stream DOC concentrations (Jardé, Gruau & Mansuy-Huault, 2007; Royer *et al.*, 2007; Molinero & Burke, 2009). Thus, cases of undetectable changes in aquatic DOC because of land-use conversion may simply reflect a balance between losing one carbon source (wetlands or SOC) but gaining another (agricultural amendments). Initial evidence for such a cancellation effect is provided by similar concentrations of dissolved organic nitrogen in streams draining human-dominated (agriculture + urban) and undisturbed, wetland-rich catchments in Wisconsin, U.S.A. (Stanley & Maxted, 2008).

Despite variability in the magnitude and direction of agricultural effects on the quantity of stream DOC, these activities appear to be consistent in altering the composition of these pools. This is not surprising, given wholesale changes in the source of the terrestrial OC pool from native vegetation to crops and organic fertilizers. Shifts in chemical composition have also been described in areas subject to forestry (Amiotte-Suchet *et al.*, 2007) and most conspicuously, in urban areas (Baker & Spencer, 2004; Aitkenhead-Peterson *et al.*, 2009). Other novel additions to the terrestrial OC pool are synthetic compounds that include biocides, antibiotics and growth hormones along with residues of genetically modified crops that are now a part of modern farming practices. In all cases, these new terrestrial sources are now routinely detectable in agricultural streams (e.g. Pedersen, Soliman & Suffet, 2005; Jardé *et al.*, 2007; Tank *et al.*, 2010b), and possible consequences of these additions are discussed below.

Finally, conversion of riparian areas to agricultural land use may have larger than expected consequences, given riparian involvement in all facets of the stream DOC regime (as a terrestrial source, terrestrial-aquatic transfer and affecting in-stream processing and production). As a source area, DOC export from the riparian zone can be a major input to streams, especially during periods of high flow in high-relief regions (e.g. McGlynn & McDonnell, 2003; Bishop *et al.*, 2004). Leaf litter can also represent a seasonally significant source of DOC in some forested headwater streams (e.g. McDowell & Fisher, 1976). In cases where buffer strips are not in agricultural production, the riparian plant community can still be substantially different from its original (native) composition, often dominated by invasive species (Tickner *et al.*, 2001). These novel assemblages often differ in rates of litter production (Ellis, Crawford & Molles, 1998) and can affect loading of bioavailable DOC to streams (Wiegner & Tubal, 2010). Overall, we expect the quantity, form and timing of DOC transfer to aquatic ecosystems to change significantly following removal or modification of riparian habitats within a catchment.

Terrestrial-aquatic transport

Hydrologic modification is a hallmark of agricultural land use and includes altered rates of evapotranspiration and infiltration, installation of drains and ditches to remove excess water from soils or construction of storage ponds and irrigation systems to provide water to crops (Fig. 2; Scanlon *et al.*, 2007; Gordon, Peterson & Bennett, 2008). Thus, flow paths that connect land to water have been re-shuffled or wholly reorganized in areas dominated by agriculture. Over the past 300 years, areas converted to pasture and rain-fed croplands have experienced large increases in discharge because of reduced terrestrial evapotranspiration (Scanlon *et al.*, 2007). Irrigation-supported agriculture, which is rapidly expanding in global extent, has opposing effects on stream flow, routinely resulting in moderate to extreme declines in discharge (Döll, Fiedler & Zhang, 2009). Inevitably, major changes in how water moves from land to water will affect the strength, timing and type of connections that transport terrestrial OC to streams.

Currently, studies that specifically examine terrestrial-aquatic linkages and DOC inputs to streams in agricultural systems are limited. The best-studied examples we are aware of focus on tile-drained crop systems that are common throughout the Midwestern U.S. and many agricultural regions worldwide. Tile drain sites contain networks of buried drainage pipes that collect soil water, lower the water table and quickly route water to the channel. The results are flashier hydrographs and increased annual water export from recipient streams (Skaggs, Brevé & Gilliam, 1994; Blann *et al.*, 2009). Floods in these systems are responsible for the majority of annual DOC export because of both increased discharge and increased DOC concentration during high flows (Dalzell, Filley & Harbor, 2005; Royer & David, 2005; Ruark, Brouder & Turco, 2009). Hence, as with water, DOC is rapidly routed from field to channel as a result of artificial drainage. Flood-dominance of inputs causes substantial intra-annual variance in stream water DOC concentrations (Stedmon *et al.*, 2006; Dalzell *et al.*, 2007). This represents a distinct departure from historical or undisturbed conditions, given that annual variance in stream DOC tends to be low and inputs of floodwater dilute, rather than enrich, the stream DOC pool in areas where wetlands persist (e.g. Hinton, Schiff & English, 1997; Gorham *et al.*, 1998).

While extensive ditching and draining are widespread in low-topography mesic environments such as the U.S. Midwest, this represents just one of many hydrologic modifications in agricultural areas. Irrigation represents another equally heavy-handed and widespread modification, with 40% of the world's food production coming from irrigated agriculture (Siebert *et al.*, 2005). These water additions can increase SOC stocks in farm fields (Denef *et al.*, 2008; Blanco-Canqui *et al.*, 2010) as well as DOC concentrations in drainage water (Hernes *et al.*, 2008; King *et al.*, 2009). However, as with tile drain systems, studies investigating effects of irrigation on stream DOC are surprisingly scarce. In short, there is a substantial knowledge gap regarding the consequences of agricultural (and more broadly, anthropogenic) modification of flow paths that connect terrestrial and aquatic environments for inputs of DOC to streams and rivers. Yet, it is clear from the studies that do exist that this re-plumbing of catchments alters the timing, magnitude, amounts and composition of aquatic DOC delivery to streams and rivers.

Aquatic processing

Studies of organic matter processing in human-dominated lotic systems are sparse, as this topic is only now beginning to receive serious research attention. Understanding DOC processing in rivers is complicated by the diversity of molecular forms and the range of physical, chemical and biological factors that affect DOC production and removal from the aquatic pool. In this section, we consider three drivers affecting DOC processing: nutrient enrichment, changes in irradiance and altered sediment inputs. Each can be strongly modified by land-use practices such as farming and urbanization (Carpenter *et al.*, 1998; Julian, Stanley & Doyle, 2008a; Hoffman *et al.*, 2010) and also has known influences on stream DOC dynamics. The relative importance of these drivers is ultimately constrained by DOC quality and water residence time, which are also strongly affected by human activities (Fig. 2).

Human activities have caused a pervasive increase in the nitrogen and phosphorus content of surface waters (Carpenter *et al.*, 1998; Smith & Schindler, 2009). Nutrient enrichment has long been known to lead to eutrophication, and greater autochthonous production should translate to greater inputs of relatively labile DOC (Bertilsson & Jones, 2003; Hilton *et al.*, 2006). This prediction has been tested in nutrient-rich agricultural streams in Indiana (U.S.A.) during summer months when dense filamentous green algal mats develop (Royer & David, 2005; Warrner *et al.*, 2009). As expected, DOC concentrations did in fact increase; however, there was no commensurate increase in DOC lability. Given that microbial respiration and organic matter degradation can also be enhanced by nutrient enrichment (Howarth & Fisher, 1976; Benstead *et al.*, 2009), labile fractions might have been rapidly consumed, resulting in no detectable change in the composition of the bulk DOC pool. This example notwithstanding, the influence of nutrient enrichment on primary production versus respiration and the overall DOC balance in human-dominated streams represents yet another substantive knowledge gap.

Insolation to streams often increases in association with agricultural land conversion because of the removal of woody riparian vegetation (Julian *et al.*, 2008b) and can change the quality and form of DOC by several mechanisms. However, the outcome of altered irradiance is likely to be difficult to predict because of confounding and offsetting processes. For example, benthic light availability can actually be lower in open-canopy agricultural streams because land-use conversion may increase the input of light-absorbing sediment (Julian *et al.*, 2008a). Further, more solar radiation may increase photosynthetic activity and associated production of labile DOC, or conversely might reduce DOC stocks and/or change its quality via photobleaching and photooxidation (Bertilsson *et al.*, 1999; Köhler *et al.*, 2002). The effect of photodegradation on DOC quality also varies between algal and terrestrial carbon sources. Tranvik & Bertilsson (2001) found that humic DOC is predominantly degraded into more labile forms when exposed to UV, whereas more labile, algal-derived DOC becomes more recalcitrant over time. Clearly, changes in irradiance can influence aquatic DOC directly and indirectly through multiple pathways, but it remains to be determined as to how these various mechanisms actually *do* play out as a result of land-use change.

In addition to modifying benthic light availability, alterations to river sediment regimes through tillage (Tiessen *et al.*, 2010) and grazing (Suren & Riis, 2010) have likely influenced DOC loads and processing in rivers by providing additional sources of, and sorption sites for DOC. Much of the sediment load contributed from cultivated areas is fine-grained (Walling & Amos, 1999), and this material can be highly effective in DOC adsorption. Sorption can occur irreversibly, creating a DOC sink (McKnight *et al.*, 2002), or reversibly, representing a potential future source to both microbes and the water column (Riggsbee *et al.*, 2008). Thus, as with light, predicting consequences of altered sediment regimes for DOC is far from straightforward, as the capacity exists for both increases and decreases in quantity and quality.

As noted in the discussion of the base case, water residence time plays a key role in constraining the degree of aquatic DOC processing, regardless of mechanism. Widespread re-engineering of river channels has altered the water residence time of river networks and thus changed the time available for different processes to influence the amount or form of DOC in fluvial systems. Most conspicuously, reservoir construction has increased the water residence time of runoff, and thereby increased the proportion of DOC loads metabolized by inland aquatic systems (Cole *et al.*, 2007). The mean age of global continental runoff at river mouth has been extended by an average of 31–58 days, with a greater than twofold increase for North America, Europe, Asia, Africa and Australia/Oceana (Vörösmarty *et al.*, 1997). Conversely, many un-impounded stream and river reaches have reduced water residence time because of the construction of canals and levees, and elimination of wetlands or floodplains which would otherwise slow water movement. Anthropogenic decreases in residence times are particularly pronounced in urban settings, where impervious surfaces result in rapid downstream routing of water by preventing infiltration into soils and ground water (Paul & Meyer, 2001). Similar hydrologic short-circuiting also occurs in agricultural areas with tile drains. Overall, streams are probably responsible for a low percentage of overall DOC uptake within surface water networks because of slow processing rates relative to water residence time (Köhler *et al.*, 2002; Kaplan *et al.*, 2008). However, uptake rates for specific simple dissolved organic compounds, including acetate (Johnson, Tank & Arango, 2009), urea and glutamic acid (Brookshire *et al.*, 2005), are comparable to rates for inorganic nutrients (Ensign & Doyle, 2006). Given the shift towards more labile forms of DOC in agricultural streams, such high uptake rates may become more common.

We have focused the above discussion on a few specific DOC-processing mechanisms that are affected by human activities, but several additional factors can also influence DOC dynamics and are undoubtedly important in different situations. For example, carbon mineralisation is temperature-dependent (Gudasz *et al.*, 2010), and altered thermal regimes are widespread among aquatic systems. Thermal pollution of rivers caused by warming of irrigation or urban runoff is a major environmental problem that can impact multiple trophic levels (Gibbons & Sharitz, 1974; McCullough, 1999). The consequences of climate-driven warming on carbon cycling are now receiving substantial attention, but more acute localised warming resulting from heated discharges and land-use change have rarely been considered in terms of effects on DOC metabolism. Other environmental drivers influencing DOC that are amplified by human land use include shifting redox conditions (e.g. in reservoirs; Bellanger *et al.*, 2004) and increased salinization of soils and surface waters (Green, Machin & Cresser, 2008), among others.

This overview of terrestrial accumulation, transfer and aquatic processing underscores opportunities for wholesale changes at all points along the continuum from OC production to its delivery and consumption or export in the aquatic environment. Further, any one process may have opposing effects in different settings or at different times of the year. Certainly, this highlights substantial uncertainty, but also important opportunities for continued investigation. Land-use changes and human perturbation are clearly altering native DOC regimes in ways we are only now beginning to recognize. And undoubtedly, future changes in land use and management will reveal new influences on aquatic DOC cycling.

What are the ecological consequences of altered stream DOC?

Changes in the magnitude, timing, quantity and form of DOC affect a broad suite of ecological variables. As the great modulator (Prairie, 2008), DOC is an energy source for microbes while also affecting other ecological patterns and processes in aquatic ecosystems. In this section, we highlight the ecological role of DOC in streams and rivers and discuss consequences of DOC change in terms of direct (i.e. via biotic use or uptake) and indirect effects on aquatic biota through its influence on light attenuation and cycling of environmental toxins.

There is substantial evidence, mostly from DOC-poor streams and rivers, that microbial growth and respiration are limited by DOC availability. Limitation has been demonstrated by increases in microbial biomass and respiration following experimental additions of labile compounds (simple sugars; e.g. Bernhardt & Likens, 2002; Wilcox *et al.*, 2005). Greater microbial production following enrichment can in turn support higher trophic levels (Wilcox *et al.*, 2005), in the same fashion that natural subsidies of terrestrial OM fuel high rates of secondary production (Wallace *et al.*, 1999). Labile carbon addition can also dramatically change microbial community composition. Although some of these experimental perturbations do not represent realistic stream conditions, we expect that similar but more subtle shifts in microbial community composition occur in response to land-use change, given that microbial communities are structured by local inputs of terrestrial DOC (McArthur, Marzolf & Urban, 1985; Koetsier, McArthur & Leff, 1997). For example, freshwater beta-proteobacteria are associated with low-molecular-weight organic matter that is increasingly abundant in agricultural and urban streams, whereas gamma-proteobacteria are associated with the higher molecular weight fractions (Foreman & Covert, 2003). However, feedbacks of altered microbial community composition on DOC cycling are not well understood.

Ecological investigations of direct uptake of DOC, particularly of terrestrially derived humic substances (HS), are generally limited to microbial studies, and it is commonly assumed that these structurally complex molecules are subject to limited biological uptake. Yet, Steinberg *et al.* (2006) draw attention to an interesting paradox regarding HS – that is, that while ecologists generally view this pool as biologically recalcitrant, biomedical researchers recognize that HS up to 1.0 kDa are taken up by organisms. Direct uptake and removal of humics from the DOC pool have a range of positive and negative effects that include reduction in rates of photosynthesis and respiration in some taxa, suppression of fungal growth, altered enzyme activities and production of heat shock proteins (Steinberg *et al.*, 2006). Given this diversity of responses that span the taxonomic range from prokaryotes to vertebrates, several authors have argued that HS should be viewed as a determinant of aquatic community structure that is of equal importance to factors such as light, temperature or nutrients (Kullberg *et al.*, 1993; Steinberg *et al.*, 2006).

As a final category of direct uptake, we include synthetic organic chemicals such as biocides. These diverse molecules represent a novel and problematic human contribution to the aquatic DOC pool that are subject to bioaccumulation, bioconcentration and metabolism (Katagi, 2010). The range of synthetic organic chemicals present in streams and rivers draining agricultural and urban areas is remarkable and includes not only biocides, but also personal care products, pharmaceuticals, hormones and flame retardants (Pedersen *et al.*, 2005). Even at sublethal concentrations, some synthetic organic chemicals stress stream biota and communities and likely alter ecosystem processes. For instance, at very low (parts per trillion) concentrations, endocrine-disrupting chemicals affected fish in the majority of Minnesota (U.S.A.) lakes where these chemicals were detected (Writer *et al*., 2010). Residues from genetically modified crops contribute an additional novel source of synthetic DOC that is common in streams adjacent to maize production (Tank *et al*., 2010b) and have been shown to reduce growth rates and increase mortality of aquatic insects (Rosi-Marshall *et al*., 2007).

The modulating role of DOC reflects multiple indirect effects of this material on aquatic processes and structure. Perhaps the most conspicuous modulation process is the control of light and water colour by terrestrially derived humic material. Light availability is particularly well studied in lake environments where the presence of HS can substantially reduce visible and UV radiation, and in turn, primary production (Hanson, Bade & Carpenter, 2003). This principle should also apply to rivers. And because UV light has deleterious effects on aquatic communities, the presence of HS offers protection to resident biota. Invertebrates appear to be more sensitive than algae, which means that the absence of HS can stimulate algal growth because UV exposure reduces densities of grazing invertebrates (Bothwell, Sherbot & Pollock, 1994).

A second well-established DOC modulation is the influence on transport and bioavailability of several toxic substances in the aquatic environment. There is a rich literature on the binding of metals to DOC, through which DOC indirectly regulates metal poisoning and bioaccumulation in food webs. In many cases, metal-DOC binding can increase the flux and bioavailability of metals to streams (Meili, 1991; Schindler *et al*., 1992). Land cover variables that typically predict stream DOC concentration have also been used to predict heavy metal accumulation in macroinvertebrates (Prusha & Clements, 2004). Alternatively, DOC-metal binding can dampen metal toxicity, such as in the case of aluminium and acid-sensitive organisms (Lacroix, 1989; Laudon *et al*., 2005). Pollutant binding to DOC is not limited to heavy metals, as it has also been reported for polyaromatic hydrocarbons (Gauthier, Seitz & Grant, 1987). Finally, ecological factors considered in this section can all interact. For example, UV light can alter DOC structure (photobleaching) and thereby affect invertebrate exposure to UV and bioaccumulation of metals (Clements *et al*., 2008). The presence of multiple stressors influenced by and including different forms of DOC has the potential to produce nonlinear changes in aquatic environments, and these shifts may be difficult to reverse through conventional management practices (Stanley, Powers & Lottig, 2010).

Managing for DOC in rivers

Prior sections have highlighted processes that may change the quantity and quality of DOC and potential ecological consequences of these changes. Cases in which stream DOC management has been a specific goal include forestry and forest management (Öhman, Seibert & Laudon, 2009) and controlling terrestrial inputs of HS to drinking water sources (Worrall, Armstrong & Holden, 2007; Varcoe *et al*., 2010). But these examples are rare, and the impacts of land management strategies on DOC are highly uncertain (Kay, Edwards & Foulger, 2009), underscoring the need for further investigation.

Most management and restoration practices have the potential to influence DOC delivery and in-stream processing, but it is unclear whether these changes will be detectable or ecologically meaningful. And even if DOC quantity and quality do change, it may or may not represent a return to the historic DOC regime. Some important questions about restoration and management are beyond the scope of the paper (e.g. How much restoration is enough? What exactly is the appropriate restoration target?), but here, we guide our discussion using a general target of trying to at least move in the direction of a more natural DOC regime and to consider the most efficient actions to move in this direction (the proverbial 'biggest bang for the buck' or 3B principle- the greatest result for the smallest effort).

A critical consideration for the success of restoration and management activities is the issue of scale. Most stream restoration projects have a small spatial extent and involve physical modification of parts of a stream channel or short channel segments (Bernhardt *et al*., 2007). Because of the large contribution of terrestrial (catchment) sources to stream DOC, smaller projects are inherently constrained in their capacity to influence DOC conditions – except perhaps in unusual cases in which autochthonous production makes a large contribution to the DOC pool (e.g. open-canopy streams) and restoration activities can re-establish appropriate rates of production. Otherwise, substantial inputs of terrestrial OC to streams means that for restoration and management efforts to be effective, they must move out of the channel and consider OC sources and delivery. To this end, the first question to consider is: does management success require a change in terrestrial OC sources across an entire basin? In the vast majority of cases, this is simply an unrealistic strategy.

Because most stream restoration projects are limited in their size but causes of impairment are usually distributed across large areas, management activities need to be carefully targeted to overcome this spatial mismatch (Diebel *et al*., 2008). For DOC management, we suggest that the best strategy is to begin with the riparian zone and expand outward as opportunities permit. Riparian management is often viewed as an optimal course of action that offers some degree of stream protection while allowing continued land use in upland areas. The efficacy of riparian buffer strips varies substantially among both different geographic settings and different response variables (Buttle, 2002), so it is by no means a cure-all. But given the reality that changing the SOC pool across the entire catchment is generally intractable and effects of in-channel modifications are likely to be small, the 3B principle points to riparian protection or re-establishment. Such a strategy re-enforces similar recommendations made for other stream response variables such as temperature, sediments and nutrients (Vidon *et al*., 2010).

Vegetated riparian areas can influence stream DOC dynamics via a number of direct and indirect pathways as discussed above, including altered DOC and POC inputs, insolation and water residence time. Further, riparian vegetation plays a key geomorphic role in dictating channel form, bank stability and sediment loading via roots and coarse woody debris supply. So what effect does maintenance or restoration of riparian habitat have on stream DOC? Not surprisingly, results are mixed.

Some restoration- and management-relevant experiments have attempted to modify POC stocks, e.g., by direct leaf litter addition or debris dam removal. While debris dam removal influenced autumnal DOC concentrations (Bilby & Likens, 1980), an opposing experiment with leaf litter additions had no effect on DOC (Aldridge, Brookes & Ganf, 2009). For streams in forested areas, leaf litter is an important, but minority source of DOC (e.g. Meyer, Wallace & Eggert, 1998), and in non-forested areas, the role of leaf litter is obviously substantially diminished. Thus, these sorts of in-stream manipulations are likely to produce only modest changes in DOC loading at best, and no persistent changes at worst.

Given the general role of riparian zones in buffering land-use effects, several studies explicitly consider how these buffers may or may not influence DOC regimes. In the case of logging, tree cutting and harvesting increase DOC inputs to surface waters in virtually all cases and regardless of the presence or absence of riparian buffer strips (reviewed by Kreutzweiser, Hazlett & Gunn, 2008). Fewer studies have considered effects of riparian management in agricultural areas, and most that do emphasise DOC exports from catchments. Consequently, their focus is on storm flows (e.g. Vidon, Wagner & Soyeux, 2008) rather than assessing typical or baseflow conditions that are of greater significance to stream biota. Buffer strip presence or composition (grass versus trees) had no measurable effects of total annual DOC exports in cropped basins in Missouri, U.S.A. (Veum *et al*., 2009), but again, the ecological significance of this result is unclear. Other flood-focused studies have reported substantial DOC inputs from intact riparian soils in otherwise human-dominated drainages (e.g. Morel *et al*., 2009). Remnant riparian areas were estimated to contribute up to 74% of storm DOC export from an urban catchment (Hook & Yeakley, 2005), leading the authors to suggest that protecting intact buffer zones is crucial for maintaining ambient carbon conditions in at least some stream settings. Finally, in contrast to its potential role as a bulk DOC source, riparian buffer strips can be highly effective at reducing pesticide loads, retaining anywhere from 30 to 99% of inputs, depending on sorption properties and pesticide type (Kay *et al*., 2009; Arora *et al*., 2010).

Wetland management represents an expanded scope of effort beyond riparian zone protection and is particularly relevant for stream DOC dynamics. These ecosystems are often major DOC sources, and as discussed above, wholesale changes in aquatic DOC regimes can be attributed to drainage of vast peatland and wetland areas, particularly in agricultural areas of North America and northern Europe. Of particular current interest is the efficacy of different peatland management practices (especially burning and drain blocking) at changing concentrations and composition of DOC in recipient streams. These restoration and management activities have important consequences beyond stream dynamics given the substantial quantity of global C storage in peatlands and worrisome evidence that these systems may be losing C in response to changes in climate and atmospheric chemistry (e.g. Turetsky *et al*., 2000). Drain blocking is now widely deployed to manage peatlands and limit DOC inputs to streams. In many, but not all cases, this practice appears to result in at least some reduction in DOC inputs, although the length of time required to effect such changes is highly variable (Höll *et al*., 2009; Ramchunder, Brown & Holden, 2009; Armstrong *et al*., 2010). Indeed, relatively rapid responses (e.g. within 1–2 years) are not expected, given that delays between restoration/management actions and biogeochemical responses are common (Hamilton, 2011).

The intent of this article was to better understand how human land use influences the quantity and form of DOC in streams and rivers, and based on this analysis, to identify management and restoration activities that address ongoing changes in stream conditions. Our perspective focuses on DOC as the chemical backbone of aquatic ecosystems, affecting multiple structural and functional components in these environments.

The first major theme of this work was that despite the central ecological role of DOC in rivers and streams, management for DOC is virtually non-existent. Second, we emphasise that land-use changes are affecting both the quantity and composition of aquatic DOC pools. In turn, the influence of this centrally important component of stream ecosystems is also expected to change, and the consequences of such alterations are highly uncertain. Relative to historic DOC regimes dominated by terrestrial inputs, many agriculturally impacted streams include a more labile DOC pool with greater inputs from crop, animal waste, autochthonous and synthetic sources. The modulating role of DOC owes largely to HS derived from terrestrial plant material, but given changes in terrestrial land cover and increased aquatic productivity, these humic materials may be declining in many streams and rivers. At the same time, synthetic DOC compounds are becoming increasingly common and are assuming novel and poorly understood ecological roles. Given these ongoing changes, our third theme was the suggestion that management actions targeting DOC should prioritize efforts in riparian zones and wetlands as the best compromise between conventional small-scale restoration projects and the large spatial scale over which OC impairment occurs in most catchments. Finally, we emphasise that given our poor understanding of the ecological consequences of these ongoing DOC changes in human-dominated basins, substantially more research and management attention needs to be directed towards this ongoing environmental transformation.

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