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The importance of the relationship between scale and process in understanding long-term DOC dynamics

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ABSTRACT

Concentrations of dissolved organic carbon have increased in many, but not all, surface waters across acid impacted areas of Europe and North America over the last two decades. Over the last eight years several hypotheses have been put forward to explain these increases, but none are yet accepted universally. Research in this area appears to have reached a stalemate between those favouring declining atmospheric deposition, climate change or land management as the key driver of long-term DOC trends. While it is clear that many of these factors influence DOC dynamics in soil and stream waters, their effect varies over different temporal and spatial scales. We argue that regional differences in acid deposition loading may account for the apparent discrepancies between studies. DOC has shown strong monotonic increases in areas which have experienced strong downward trends in pollutant sulphur and/or seasalt deposition. Elsewhere climatic factors, that strongly influence seasonality, have also dominated inter-annual variability, and here long-term monotonic DOC trends are often difficult to detect. Furthermore, in areas receiving similar acid loadings, different catchment characteristics could have affected the site specific sensitivity to changes in acidity and therefore the magnitude of DOC release in response to changes in sulphur deposition. We suggest that confusion over these temporal and spatial scales of investigation has contributed unnecessarily to the disagreement over the main regional driver(s) of DOC trends, and that the data behind the majority of these studies is more compatible than is often conveyed.

1. Introduction

There have been widespread observations of increased dissolved organic carbon (DOC) concentrations in surface waters across parts of Europe and North America over the last two decades (Driscoll et al., 2003; Worrall et al., 2004; Evans et al., 2005; Skjelkvale et al., 2005). This has raised concerns about drinking water treatment and the production of carcinogenic byproducts (Gallard and von Gunten, 2002; Holden et al., 2007), and the further possibility that climate change is causing degradation of soil carbon stores (Freeman et al., 2001a; Bellamy et al., 2005). In both cases there is a common perception that DOC increases are likely to be environmentally detrimental, and increasingly land managers are seeking guidance from the scientific community with respect to practical methods to control or even reverse these trends.

Several hypotheses have been put forward to explain increasing DOC trends (Table 1). One hypothesized driver for increasing DOC trends is a long-term change in the chemistry of atmospheric deposition that has been recorded across many of these areas as a result of reductions in anthropogenic sulphur and, in some locations, seasalt deposition (Evans et al., 2006; Vuorenmaa et al., 2006; de Wit et al., 2007; Monteith et al., 2007; Dawson et al., 2009; Hruska et al., 2009; Oulehle and Hruska, 2009). However, others have rejected this hypothesis, arguing that DOC trends are more consistent with changes in rainfall, temperature and/or atmospheric carbon dioxide (CO_2) than declining atmospheric sulphur deposition (Worrall and Burt, 2007a; Eimers et al., 2008c; Lepisto et al., 2008; Sarkkola et al., 2009), building on earlier studies suggesting relationships between these drivers and increased DOC (Freeman et al., 2001a; Freeman et al., 2004; Hongve et al., 2004; Fenner et al., 2007). Some reject the deposition hypothesis outright as DOC concentrations have decreased in some areas where acid deposition has declined (Clair et al., 2008). Other drivers have also been suggested; these include changing nitrogen deposition (Findlay, 2005), solar radiation in boreal lakes (Hudson et al., 2003), and land management practices (Yallop and

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Table 1
Summary of published research about long-term trends in DOC concentrations. Sites are typically 'acid sensitive', with range of soils (peat, podzols and mineral soils) with forest and/or moorland vegetation cover. Countries are Canada (CA); Czech Republic (CzR); Finland (FI); Norway (NO); Sweden (SE); United Kingdom (UK); United States of America (USA). *Significant monotonic trend that is either increasing (+), decreasing (-) or has no significant trend (nt). Information not reported (nr). Acid deposition quantified in terms of sites with 'high' (H) or 'low' (L) deposition. Text typed in italics is information based on authors knowledge and not reported in the specific paper. Water body is classified as lake (L) or stream (S). Statistical methods are summarized as: Seasonal Kendall test and Sen slope (SKT); Mann-Kendall test and theil slope (MKT); correlation (C); linear regression (LR); multiple linear regression (MLR); mixed-effect model (MEM); process-based model (PM); artificial neural network (ANN); Student's T-Test (TT). Table rows are ordered in terms of disagreement, agreement or no mention of acid deposition hypothesis as driver of DOC trends. NB this is a summary of research and does not include all papers published on DOC trends.

Paper	Region	No. Site	DOC trend*			Driver of trend							Catchment			Monitoring			Statistical method
			+	nt	-											Time period		Sample frequency	
						Seasalt dep.	Acid dep.	Nitrogen enr.	Atmos. CO_2	Temperature	Preip./ runoff	Management	Historic acid deposition	Area (km^2)	Lake/ stream	Start	End		
Freeman et al. (2001a)	UK	22	20	2	0		✗			✓		✗	*H–L*	*0.5–16*	L/S	1988	2000	1–3 month	SKT
Hudson et al. (2003)	CA	9	nr	nr	nr		✗			✗	✓		nr	0.9–5.9	L	1978	1998	5–24/year	MLR
Hongve et al. (2004)	NO	24	24	0	0					✗	✓		*H*	0.1–9	L	1983	2001	>1 year	TT
Worrall et al. (2004)	UK	198	153	45	0		✗	✓		✓	✓	✓	H–L	0.04–2100	L/S	1961/	2000	nr	SKT
Striegl et al. (2005)	USA	1	0	0	1					✓			L	831400	S	1978	2003	6–8/year	ANCOVA
Worrall and Burt (2007b)	UK	315	216	44	55		✗		✓	✓	✓		H–L	nr	L/S	1962/	2002	1–4 weeks	SKT/ MLR
Clair et al. (2008)	CA	3	0	1	2		✗						L	17–297	S	1983/	2004	1 week	SKT
Eimers et al. (2008a)	CA	7	6	1	0		✗	✗		✗	✓		nr	0.1–1.9	S	1980	2001	1–2 weeks	MKT/MLR
Lepisto et al. (2008)	FI	1	0	1	0		✗			✓	✓	✗	L	3160	S	1962	2005	~3–1month	MKT
Sarkkola et al. (2009)	FI	8	7	1	0		✗			✓	✓		L	0.2–4.9	S	1979	2006	<1–4weeks	SKT/MEM
Hejzlar et al. (2003)	CzR	1		0	1		✓						H	438	S	1969	1983	1 day	SKT; MLR
			1				✓			✓	✓					1984	2000		
Findlay (2005)	USA	1	1	0	0		✓	✓		✗	✗	✗	H	21 000	S	1988	2003	1–4 weeks	LR
Evans et al. (2006)	UK	11	11	0	0	✓	✓			✓	✗		*H–L*	*0.5–16*	L	1988	2003	3 month	MLR
Vuorenmaa et al. (2006)	FI	13	10	3	0		✓				✗		nr	0.3–4.36	L	1987	2003	1 month	SKT/C/MLR
de Wit et al. (2007)	NO	3	1	2	0		✓			✗	✗		H	0.4–0.8	S	1985	2003	1 week	SKT/MLR
Monteith et al. (2007)	UK, SE, NO, FI, USA, CA	522	363	20	139	✓	✓			✗	✗		*H–L*	nr	L/S	1990	2004	nr	SKT/MLR
Erlandsson et al. (2008)	SE	28	nr	nr	nr	✗	✓			✗	✓		*H–L*	210–26800	S	1970	2004	1 month	MKT/MLR
Futter et al. (2008)	FI	1	1	0	0		✓			✓	✓		L	0.3	L/S	1992	2001	nr	PM/ANN/ MKT
Dawson et al. (2009)	UK	2	2	0	0		✓			✗	✗		*H–L*	nr	S	1986	2007	~1 week	MEM
Hruska et al. (2009)	CzR	2	2	0	0		✓			✗	✗		H	0.2–0.3	S	1993	2007	1 week	LR/ SKT
Oulehle and Hruska (2009)	CzR	11	9	2	0		✓			✗	✗	✗	H	8–74	L/S	1969	2006	~1 month	SKT/MLR

Clutterbuck, 2009). In the UK uplands, an increase in heather burning has coincided with an increase in DOC concentrations (Yallop et al., 2006; Yallop and Clutterbuck, 2009) and restoration practices such as blocking of artificial drainage ditches are being carried out with the intention of reducing DOC concentration at source prior to drinking water treatment (Wallage et al., 2006; Armstrong et al., 2009).

Long-term trends in DOC concentrations (typically representing change over the last two decades) can be orders of magnitude smaller than spatial and seasonal variation (Table 2), making it difficult to detect weaker trends (Fig. 1). Several studies have shown that much of the larger seasonal and spatial variability can be explained by processes and catchment characteristics controlling the availability of soluble organic matter and subsequent hydrologic transport (e.g. McDowell and Likens, 1988; Hope et al., 1997; Laudon et al., 2003; Clark et al., 2007b). It is clearly necessary to distinguish between cause-effect relationships influencing the spatial and seasonal variability in DOC from those influencing long-term changes if drivers of long-term trends are to be correctly identified. Any factors invoked to explain long-term change must also show (either individually or in combination) an appropriate long-term trend. Otherwise, there is a risk that analysis will confuse variables explaining larger spatial and seasonal variance with those responsible for smaller changes in the annual level (i.e. mean annual concentration).

2. A unified hypotheses for long-term DOC dynamics

2.1. Conceptual model of DOC dynamics in surface waters

DOC concentrations in surface waters at any one site can be expressed using a time series model. In a general model, the variation in the data can be decomposed in to a series of components describing the level or overall mean value (α), long-term trend (T), seasonal component (S) and random noise (N) (Chatfield, 1984). For a specific DOC time series model, an additional term accounting for inter-annual variation (IAV) is added, such that the generic model for DOC concentrations in surface waters at time t in location l becomes:

$$DOC_{tl} = \alpha_l + T_{tl} + S_{tl} + IAV_{tl} + N_{tl} \quad (1)$$

This model underpins the synthesized time series shown in Fig. 1 and some of the components are represented in Table 1. The term α will vary with location (l) due to differences in catchment characteristics such as soil and vegetation and long standing land management practices. S and IAV are driven principally by variations in temperature, precipitation, sea salt deposition (in maritime regions) and snow melt (in high elevation and/or high latitude areas) and N represents short-term rainfall events. S, IAV and N will also vary in magnitude between location depending on soil and catchment properties (e.g. peatland or forested sites). T can be driven by any factor affecting the processes of DOC production, solubility or transport over a long-term time scale. T may also vary between locations due to inherent catchment properties, management strategies or the magnitude of change in the external driver(s) of DOC processes.

2.2. Hypotheses for driver(s) of long-term DOC trends

As noted above, hypothesized driving variables of long-term DOC trends (T_{tl}) have included; acid sulphur deposition (T_a); seasalt deposition (T_{ss}); nitrogen deposition (T_n); temperature (T_{tp}); precipitation (T_p); atmospheric CO_2 (T_{CO_2}) and land management (T_m). Therefore, the trend at any one location can be seen as a combination of one or more of these drivers:

$$T_{tl} = T_{tl,a} + T_{tl,ss} + T_{tl,n} + T_{tl,tp} + T_{tl,p} + T_{tl,CO_2} + T_{tl,m} + \ldots. \quad (2)$$

We argue that the principle driver of DOC trends (whether these trends show an overall monotonic increase, decrease or no change with time) over the last two decades varies spatially with location. In regions where acid deposition has been high, DOC trends have been driven mainly by declining pollutant sulphur and seasalt deposition, and these trends have been greater than trends driven by other factors such as climate change (e.g. Fig. 1f,h):

$$T_{tH,a} + T_{tH,ss} > T_{tH,n} + T_{tH,tp} + T_{tH,p} + T_{tH,CO2} + T_{tH,m} + \ldots\ldots \quad (3)$$

Where H refers to locations in high deposition areas and t is the last two decades. In regions where acid deposition has been low, acid deposition is unlikely to be the main driver of DOC trends, such that:

$$T_{tL,a} + T_{tL,ss} < T_{tL,n} + T_{tL,tp} + T_{tL,p} + T_{tL,CO_2} + T_{tL,m} + \ldots\ldots \quad (4)$$

Where L refers to locations in low deposition areas and t is the last two decades. Therefore, other factors may influence DOC trends in low deposition areas (e.g. climate change), although the magnitude of these trends may, in some cases, be too small to detect over seasonal and inter-annual variability (e.g. Fig. 1e,g) and could also counteract each other.

In addition to the wider regional differences caused by historic deposition loading, some specific locations may not respond to changing acid deposition because soil and surface waters are well buffered against changes in acidity. Therefore, T_a and T_{ss} can vary in magnitude between different locations with similar sulphur deposition loading. If land management has changed over the period studied, it may impact on DOC trends within specific catchments where intervention has occurred, and may or may not cause comparatively large value for T_m at a specific location. However, if land management has remained static over the period of interest, its impact is most likely to be seen in terms of influencing the magnitude of the overall mean concentration or level (α) and perhaps the amplitude of the seasonal cycle (S).

Table 2
Example of variations in surface water DOC concentrations with spatial and temporal scale (1993–2007). Data from Acid Waters Monitoring Network (AWMN) and Environmental Change Network (ECN). Spatial variation illustrated with overall level and range in concentrations between sites. Seasonal range shows the difference between the mean summer/autumn concentrations (July, August, September) when DOC is at a maximum and mean winter/spring concentrations (February, March, April) when DOC is at a minimum. Seasonal range is less than the total range of concentrations seen within a year. Trend shows the Theil slope estimate for the annual median concentrations. AWMN stream waters were sampled monthly.

Site	Location	Overall level and range (mg DOC/L)		Seasonal range (mg DOC/L)		Trend (mg DOC/L/yr)
		Median	Min–Max	Median	Min–Max	
Dargall Lane Burn	−4.43E 55.08°N	2.0	0.1–8.5	1.2	−0.4–3.5	0.06
Allt na Coire nan Con	−5.61E 56.76°N	4.7	1.1–13.4	4.7	1.9–7.3	0.16
Coneyglen Burn	−7.01E 54.74°N	9.2	1.7–28.8	8.3	−2.4–12.1	0.15
Beagh's Burn	−6.18E 55.12°N	13.6	3.3–37.0	13.3	4.8–28.8	0.34
Cottage Hill Syke[a]	−2.38E 54.69°N	17.6	3.5–41.5	16.2	11.1–24.6	0.10

[a] ECN weekly data were resampled every month to be consistent with AWMN data.

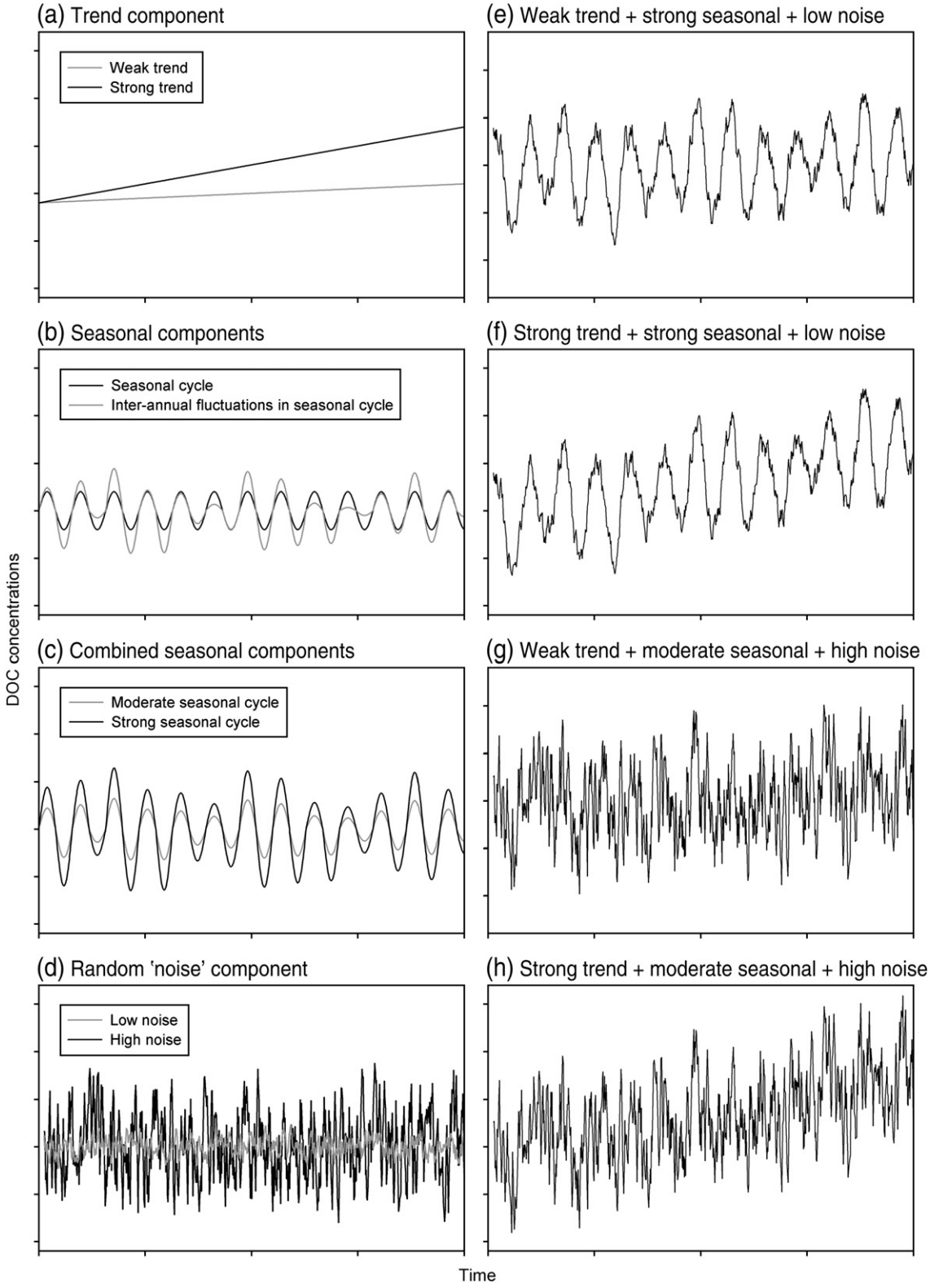

Fig. 1. Synthetic time series to show how large seasonal and intra-annual variation can mask a weak long-term trend. Time series components used to generate each synthetic time series are: (a) weak and strong linear trend (*T*); (b) regular seasonal cycle (*S*) and random inter-annual seasonal fluctuations (*IAV*) (e.g. to recreate wet and dry years); (c) combined seasonal cycle and random variation adjusted to show a strong and moderate cycle (*S* + *IAV*); (d) weak and strong random noise (*N*). Synthetic time series produced are representative of a typical British (e,f) moorland peatland stream, with low noise and strong seasonal cycle, and (g,h) forested (organo-mineral soil) stream with high noise and moderate seasonal cycle. In both streams, the noise represents fluctuations that would be expected due to changes between base and storm flow.

It should also be noted that interactions may exist between catchment properties (such as soil type and land management) and/or the different drivers of DOC trends, such that a multiplicative time series model rather than simple additive model is more appropriate. These details aside, the simple additive models (Eqs. (1, 2, 3 and 4)) illustrate how 'competing' theories about long-term DOC dynamics

can be understood as a set of potentially complementary mechanisms describing how various spatial and temporal factors affect the processes of DOC production, solubility and transport at different locations and under different conditions (Table 3). These relationships are discussed in more detail in the following sections.

3. Process controls on DOC: biology, chemistry and hydrology

DOC production in terrestrial systems is a biological process. Low-molecular weight highly degradable DOC is released by plant roots, soil and aquatic microorganisms, whereas high-molecular weight coloured aromatic and refractory DOC is released during decomposition of organic material (Thurman, 1985). Release of labile DOC in plant root exudates is thought to stimulate decomposition and release of high-molecular weight DOC from soil organic matter (Kuzyakov, 2002; Freeman et al., 2004). Therefore, biological DOC production and consumption is controlled by factors affecting soil organisms (e.g Cole et al., 2002), enzymes (e.g. Freeman et al., 2001b) and plant growth (e.g. temperature, moisture, nutrient availability, and atmospheric CO_2), the quality of the DOC released and its biodegradability (Kalbitz et al., 2003), and the quality of the solid substrate to be decomposed. Generally, DOC concentrations are greatest in freshwaters draining soils with high organic matter content and high C:N, i.e. nutrient poor systems where production of organic material is greater than decomposition (Aitkenhead and McDowell, 2000).

Chemical processes and properties affect whether organic carbon 'dissolves' in water, in addition to influencing biological activity. Organic carbon solubility is controlled by surface functional groups; organic carbon dissociates by releasing protons (H^+) and forms a negatively-charged soluble species. This process is regulated by chemical variables, particularly pH and ionic strength of the soil solution and the presence of polyvalent cations like aluminum ($Al3^+$). The degree to which DOC is influenced by these chemical properties depends on its molecular structure. Two general chemical groups are: humic substances (humic and fulvic acids) derived from plant material that are not easily utilized by microorganisms and non-humic substances like proteins and sugars that are easily consumed by microorganisms (Thurman, 1985). Humic acids are typically the coloured aromatic fraction seen in freshwaters (Thurman, 1985; Weishaar et al., 2003), and can be removed during water treatment using coagulants like $Al3^+$ (Exall and Vanloon, 2000). Increased ionic strength, and the associated input of polyvalent cations, also causes coagulation and precipitation of organic carbon, particularly humic acids. The sensitivity of humic acids to pH is utilised in standard analytical procedure used to separate humic substances, as acidification to pH 2 will cause humic acids to precipitate whereas fulvic acids will remain in solution (Aiken et al., 1985). Increased acidity has also been shown to slow biological activity and the production of DOC (Andersson et al., 2000), while increased inputs of nitrogen may increase biological productivity (Bragazza et al., 2006), and inputs of acid anions like sulphate (SO_4^{2-}) and nitrate (NO_3^-) to wetland soils can result in DOC consumption during redox reactions (Bartlett et al., 2005).

Like chemical factors, hydrology has both a direct and indirect control on DOC. Direct control occurs via the influence of hydrology on the soil residence time and routing of DOC from soil to stream. In organo-mineral soils, DOC transport increases as the water flow path shifts from baseflow through the mineral soil layer (where DOC is retained) to storm flow through the upper organic soil layers and litter (where DOC is produced) resulting in an increase in DOC with storm discharge (McDowell and Likens, 1988). In peats, DOC concentrations are generally greater, and dilution or no change in DOC may occur during storm events (Schiff et al., 1998; Laudon et al., 2004; Clark et al., 2007a; Eimers et al., 2008a). However, irrespective of changes in concentration, DOC flux increases with rainfall and runoff (Hope et al., 1997) as the increased volume of water during runoff events is typically several orders of magnitude greater than any dilution that may occur (Clark et al., 2007a). Changes in water volume also influence the concentration/dilution of DOC, such that increases in DOC concentration due to 'evapo-concentration' have been observed in soils (Waiser, 2006), and decreases in DOC concentrations have been noted for volume-weighted mean concentrations relative to the observed mean values (Eimers et al., 2008b). Indirect effects of hydrology on DOC include the influence of water content on biological production and/or biogeochemical cycling and chemical controls on solubility. In peats, increased DOC concentrations have been noted after periods of prolonged drought (Watts et al., 2001). However, episodic water table draw-down during drought periods (Clark et al., 2005) and long-term draw-down caused by erosion gullies (Daniels et

Table 3
Scale of spatial and temporal variation in drivers of DOC production, solubility and transport.

Driver		Process			Spatial Scale				Temporal Scale					
		Production	Solubility	Transport	Global	Regional	Catchment	Site	Millennia to Centuries	Decadal	Inter annual	Seasonal	Episodic
Ecosystem properties	Geology		✓	✓			↔		↔				
	Topography			✓			↔		↔				
	Soil (inc. wetland)	✓	✓	✓			↔		↔				
	Vegetation	✓					↔		↔			↔	
Climate/ Weather	Temperature	✓			↔					↔		↔	
	Rainfall	✓	✓	✓		↔		↔		↔			↔
	Snow			✓		↔		↔		↔			↔
Atmospheric deposition	Nitrogen	✓	✓			↔				↔			
	Sulphur	✓	✓			↔				↔			
	Chloride		✓			↔				↔			
	'Seasalt'		✓			↔				↔			↔
Land management	Forestry	✓	✓					↔		↔			↔
	Drainage	✓	✓	✓				↔		↔			↔
	Controlled burning	✓						↔		↔			↔
	Liming	✓	✓					↔		↔			↔

al., 2008) has been associated with decreased DOC due to sulphide oxidation to SO_4^{2-} and the associated soil water acidification and decline in DOC solubility.

4. Scale controls on DOC: spatial and temporal (seasonal, short-term inter-annual and long-term trend)

Variation in the spatial and temporal scale of the drivers of the processes of DOC production, solubility and transport are summarized in Table 3. Catchment factors determine whether conditions are appropriate for DOC production and subsequent export to surface waters. Fundamentally, DOC cannot be exported to surface waters if it is not produced, therefore, biological production provide a primary control on freshwater DOC. Since DOC is produced through incomplete decomposition of organic matter, it tends to be produced in wet, cool and/or nutrient poor areas where decomposition is limited, and soil organic matter content and C:N ratios are high (Aitkenhead and McDowell, 2000). Spatial variation in the composition of soils, vegetation, geology and topography will also affect the hydrological and chemical regulation of DOC solubility and transport. Perhaps the most consistent finding between studies of spatial controls on DOC loss has been a clear correlation between DOC concentrations and fluxes and the area of wetland/peatland in a catchment (e.g Hope et al., 1997; Laudon et al., 2003; Creed et al., 2008). As areas with cool and wet climates are associated with organic soil development, and these organic rich soils release the greatest amount of DOC, DOC concentrations in surface waters will also show a good correlation with respect to spatial variations in rainfall and temperature (Tranvik and Jansson, 2002). Land management practices may also vary spatially, such that sites with artificial drainage ditches (Wallage et al., 2006), heather burning (Yallop and Clutterbuck, 2009) and forest management (Grieve and Marsden, 2001; Neal et al., 2001) may have elevated DOC concentrations relative to undisturbed sites. However, land management does not always have a significant impact on freshwater DOC concentrations (Worrall et al., 2007a; Worrall et al., 2007b), so the actual response to management is likely to depend on particular site characteristics. Although important, spatial factors cannot necessarily explain changes in DOC over time (Evans et al., 2002).

Another consistent observation regarding DOC dynamics is a clear seasonal cycle in many surface waters, which is often linked to biological production and hydrological export of DOC. For a catchment with high DOC concentrations, the seasonal variation in DOC is perhaps the largest source of variation (Table 1). In peats (Fig. 1e,f), where there is little change in stream water DOC with flow, seasonality generally tends to follow the seasonal pattern in temperature linked to biological production of DOC (Clark et al., 2005; Billett et al., 2006; Koehler et al., 2009). In catchments with organo-mineral soils or mixed soils (Fig. 1g,h), seasonality can be strongly influenced by the hydrological regime, such that irregular variation in flow can mask the seasonal temperature driven cycle in temperate regions (Dawson et al., 2008) or create seasonal peaks in DOC exports during spring snowmelt periods in boreal regions (Laudon et al., 2003; Buffam et al., 2007). Inter-annual variability in rainfall can accentuate the seasonal hydrological response such that the amplitude of the seasonal cycle changes between wet and dry years (Fig. 1), which can account for a significant proportion of the variance in DOC concentrations between years (Vuorenmaa et al., 2006; Erlandsson et al., 2008). Seasonal variation in seasalt deposition in maritime areas can also be linked with seasonality in DOC, as inputs of chloride (Cl^-) are associated with increased mineral acidity during winter periods (Chapman et al., 2008).

Trend is the long-term variation in DOC over several years (Fig. 1a), and is typically one to two orders of magnitude lower than the seasonal variation in DOC at a particular site, and also lower than the spatial variation between sites (Table 1). A monotonic trend can range from linear to distinctly non-linear but will always be in a single direction. A trend may also represent a long-term oscillation that can occur over decadal time scales (e.g. Erlandsson et al., 2008). Importantly, the widely reported DOC trends across many sites in Northern Europe and North America (Monteith et al., 2007) over the last two decades are monotonic. Hence, any factor controlling DOC production, solubility or transport that has also displayed a monotonic trend across these regions could drive long-term DOC concentrations. Possible regional drivers with an increasing or decreasing monotonic trend include temperature (Freeman et al., 2001a), atmospheric CO_2 (Freeman et al., 2004) and sulphur deposition (Monteith et al., 2007). Over the past two decades in the UK and southern Scandinavia there has also been a long-term trend in seasalt deposition resulting primarily from a period of exceptionally high seasalt inputs in the late 1980s–early 1990s (Evans et al., 2001) that has not yet recurred. A significant reduction in Cl^- emissions (Dore et al., 2008) is also likely to have led to a reduction in acid Cl^- deposition in regions close to major coal-burning sources. Year-to-year variation in rainfall is common, but few regions experiencing long-term increases in DOC concentrations show any indication of monotonic trend in annual rainfall (Evans et al., 2006; Oulehle and Hruska, 2009) although significant increases in winter precipitation have been noted in Finland (Sarkkola et al., 2009).

5. Confusion of spatial and temporal scale

As noted above, DOC dynamics within soil and stream waters are controlled by a number of different factors that influence the production, solubility and transport at a range of spatial and temporal scales (Table 3). As many of these drivers vary over both spatial and temporal scales, it is not easy to attribute change in a particular driver to the appropriate components of the DOC time series (Eq. 1). Therefore, correct identification of the factors that account for the majority of the variation in DOC depends on the spatial and temporal scale of DOC variation studied. It is possible that conflicting explanations for drivers of DOC trends have arisen in part because of confusion over the scale of investigation. As seasonal and spatial variation in DOC concentrations are orders of magnitude greater than the trend (Table 1), any analysis of the raw data alone is likely to find that spatial and seasonal drivers explain more of the variance as there is simply more seasonal and spatial variance to explain. For instances, in analysis of Canadian catchments, Eimers et al. (2008c) suggested an inverse relationship between SO_4^{2-} and DOC arises from seasonal variation in catchment hydrology and source waters; where high DOC-low SO_4^{2-} waters from wetlands dominate in summer and autumn and low DOC-high SO_4^{2-} waters from upland organo-mineral soils dominate in spring. They argued that these seasonal relationships due to catchment hydrology rather than chemical solubility could explain long-term trends seen elsewhere. In a study of eight Finnish catchments, Sarkkola et al. (2009) found that the area of peatland was the most significant explanatory variable of annual and seasonal TOC concentrations followed by precipitation and temperature. Together these factors explained 56–71% of the seasonal and annual variance but the extent to which they were able to explain long-term DOC increase was not addressed. Although long-term monotonic trends in temperature, winter precipitation and acid deposition were also noted alongside increasing DOC concentrations, the area of peatland and annual and summer rainfall (which displayed no long-term monotonic trend) were the most significant explanatory variables. No significant relationship between DOC increases and declining atmospheric deposition was found, however, deposition at these sites was lower than other sites where relationships between deposition and DOC have been found (Table 1). Hence in a spatial–temporal analysis, explanatory variables with large spatial, and inter-annual variation were more significant in explaining variation in the whole time series than potential drivers of smaller magnitude long-term trends.

Where relationships between declining in sulphur or seasalt deposition and increasing in DOC has been found, analysis has usually been carried out using surface water SO_4^{2-} or Cl^- concentration data where seasonality was removed (Evans et al., 2006; Oulehle and Hruska, 2009) and the spatial variation in DOC concentrations between sites was reduced by considering the percentage change in DOC rather the absolute value (e.g. Monteith et al., 2007). Hence, the other spatial and temporal factors known to influence DOC were removed from the data. The hypothesis suggests that acid deposition has caused long-term suppression of 'naturally' variable DOC concentrations, reducing overall annual concentrations in catchments with organic rich soils where DOC concentrations would be high. The mechanism would also be expected to decrease the magnitude of the seasonal cycle driven by temperature and rainfall, as chemical changes in solubility would decrease organic carbon solubility throughout the year. This does not exclude roles of other factors such as soil and vegetation in affecting DOC spatially, or temperature and hydrology in affecting DOC seasonally; acid deposition could have simply 'dampened' the DOC response to these other drivers in these catchments. Other analyses support the idea of multiple temporal scale drivers, with both dynamic modelling and statistical approaches showing that seasonal and short-term inter-annual variation can be explained by climate whereas long-term variation can be attributed to changes in atmospheric deposition (Vuorenmaa et al., 2006; Erlandsson et al., 2008; Futter and de Wit, 2008; Oulehle and Hruska, 2009).

In many recent studies, attention has largely focused on separating out drivers as if they are independent of each other, or indeed competing. However, it is also possible that there may be an interaction between drivers such that the product of changes in both of the drivers is greater than the effect of each individual driver alone. For instance, changes in temperature and CO_2 (Fenner et al., 2007) and temperature and water table draw-down (Clark et al., 2009) have shown significant interaction and impact on net DOC production in laboratory experiments. It is possible that changes in temperature, precipitation and acid deposition could also show an interaction with biological activity and hence DOC production. Such interactions could modify the structure of the additive time series model (Eqs. (1, 2, 3, 4)), as mentioned above.

Spatially, there is no reason to assume catchments with different soils, vegetation cover and land management practices will all show an identical response to broad-scale regional drivers like declining acid deposition. High water tables, SO_4^{2-} reduction and the associated attenuation of acidity (Morgan, 1995; Bottrell et al., 2004) may render peatland areas insensitive to changes in sulphur deposition where the deposition loading has been lower than the natural rate of biological SO_4^{2-} reduction (Clark, 2005). For instance, no significant monotonic DOC trend was observed in a peatland stream (Clark et al., 2005) during a period when significant increasing trends were observed in other British catchments with mixed organic soil types (Freeman et al., 2001a); soils and waters where buffering is mainly by the bicarbonate system rather than organic acids, are also likely to show no response to changes in acid deposition. Monteith et al. (2007) show that base cation status governs the sensitivity of the DOC response to deposition between catchments. Likewise, remote areas with little history of acid deposition may not show the same trends as those in industrialised regions (e.g. Striegl et al., 2005), or changes in deposition may be so low and/or seasonal and short-term inter-annual variations (e.g. rainfall, episodic drought-induced acidification) so large that they mask any long-term deposition-driven trend e.g. (Fig. 1) (Hudson et al., 2003; Clark et al., 2005; Eimers et al., 2008c; Sarkkola et al., 2009). Conversely, it may be difficult to detect a long-term climate signal in highly polluted areas where it is masked by a much stronger acid deposition signal. This observation appears key in explaining the contrasting conclusions reached about drivers of long-term DOC change between those working in some of the most polluted areas advocating a link with deposition (e.g. Evans et al., 2006; de Wit et al., 2007; Oulehle and Hruska, 2009) and those working in some of the least polluted areas advocating climate (e.g. Clair et al., 2008; Lepisto et al., 2008; Sarkkola et al., 2009).

6. Conclusion

Given the spatial heterogeneity between catchments and the difference between factors driving seasonal, short-term inter-annual and longer-term temporal variation, most of the explanations of DOC dynamics are potentially compatible with each other. In acid impacted regions, we believe that long-term trends in DOC over the last two decades have been driven principally by declining atmospheric deposition; but this explanation of long-term trends does not exclude other spatial and temporal factors contributing to the overall variability in DOC concentration. As levels of sulphur deposition begin to approach background levels it is likely that longer-term changes in the climatic drivers that currently describe much of the within-year and short-term between-year variability will dictate the direction of future DOC trends. Rather than being in conflict with each other, we suggest that these contrasting studies are contributing to a wider unified understanding of local to regional scale spatial variability of DOC dynamics with respect to multi-scale temporal drivers.

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