

## Cross-regional prediction of long-term trajectory of stream water DOC response to climate change

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[1] There is no scientific consensus about how dissolved organic carbon (DOC) in surface waters is regulated. Here we combine recent literature data from 49 catchments with detailed stream and catchment process information from nine well established research catchments at mid- to high latitudes to examine the question of how climate controls stream water DOC. We show for the first time that mean annual temperature (MAT) in the range from  $-3^{\circ}$  to  $+10^{\circ}$  C has a strong control over the regional stream water DOC concentration in catchments, with highest concentrations in areas ranging between  $0^{\circ}$  and  $+3^{\circ}$  C MAT. Although relatively large deviations from this model occur for individual streams, catchment topography appears to explain much of this divergence. These findings suggest that the long-term trajectory of stream water DOC response to climate change may be more predictable than previously thought. **Citation:** Laudon, H., J. Buttle, S. K. Carey, J. McDonnell, K. McGuire, J. Seibert, J. Shanley, C. Soulsby, and D. Tetzlaff (2012), Cross-regional prediction of long-term trajectory of stream water DOC response to climate change, *Geophys. Res. Lett.*, 39, L18404, doi:10.1029/2012GL053033.

### 1. Introduction

[2] Dissolved Organic Carbon (DOC) is one of the most critical water quality parameters in natural freshwaters. It plays a vital role as a transport vector for metals and organic pollutants, energy substrate for aquatic organisms and as a modulator of the aquatic food web structure. Increasing DOC concentrations and fluxes in surface waters observed across extensive areas of the northern hemisphere [Monteith

*et al.*, 2007] have resulted in large research efforts to better understand the causes and effects of stream water DOC dynamics. Improving our understanding of what controls DOC export is of vital importance to the ecology and management of watersheds as increasing DOC concentrations lead to water quality degradation and increasing costs for drinking water purification [Kaplan *et al.*, 2006], but also because of the role of DOC in the ecosystem C balance [Cole *et al.*, 2007]. While the production and export of DOC from the terrestrial landscape has been extensively studied during the past several decades in mid- to high latitude regions, fundamental understanding of processes that control stream water DOC across climatic regions is still lacking. The lack of such understanding of how stream water DOC is regulated by climate is especially important for northern catchments where air temperature increase will likely be greatest [Denman *et al.*, 2007].

[3] It is well established that much of the intra-regional variability in DOC concentrations is controlled by wetland cover in the upstream catchment [Creed *et al.*, 2008]; however, this landscape feature alone does not explain the spatial variability of DOC observed across the north. Despite generally lower DOC concentrations from mineral soils, the largest flux on a regional scale is from mineral soil dominated areas because of their areal dominance in most high-latitude landscapes [Ågren *et al.*, 2007]. Therefore the key to elucidating the controls on DOC concentrations at the regional scale lies in the underlying processes by which non-wetland areas feed DOC to adjacent aquatic systems. This is not only essential for disentangling the causal mechanisms of the recent DOC concentration increase, but also for our ability to foresee how DOC concentrations in small streams and lakes may respond to environmental perturbations in the future.

[4] DOC originates from the incomplete decomposition of organic material. Hence, soil organic matter (SOM) is the main source of DOC in both peat-dominated wetlands and more extensive, drier upslope areas. In mineral soil-dominated catchments, these SOM pools occur either as a humus layer overlying the parent material or as organic rich riparian soils [Lyon *et al.*, 2011]. Although the complexity of SOM accumulation makes the mechanistic understanding far from complete, the formation of organic soils is mainly conditioned by interrelated environmental and biological factors [Schmidt *et al.*, 2011]. Generally, the largest accumulation of SOM occurs where the soil and climatic conditions are such that Net Primary Production (NPP, resulting in litter accumulation) exceeds the rate of organic matter mineralization. However, the relative accumulation of SOM pools in a catchment alone does not explain the spatial patterns of DOC in surface waters. Transport mechanisms and hydrological connectivity between the sources of SOM and

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**Table 1.** Details of the Literature Data Including Mean Annual Temperature (MAT), Average DOC Concentrations and References<sup>a</sup>

	Location	Catchment Name	MAT C°	DOC (mg L <sup>-1</sup> )	Reference
1	Alaska	High permafrost	-2.5	7.03	<i>Petrone et al.</i> [2006]
		Medium permafrost	-2.5	3.33	
		Low permafrost	-2.5	3.54	
2	Swedish Lapland	A7	-1	10.4	<i>Olefjeldt</i> [2011]
		B2	-1	9.2	
		Abiskojokk	-1.5	1.7	
		Viepsajokka	-1.7	3.2	
		Y1 Kihlankjokki	-0.5	7.3	
3	Kola Peninsula, Russia	Kola 3	-1.5	9.0	<i>Pekka et al.</i> [2004]
		Kola 4	-1.5	11.0	
		Kola 9	-0.5	9.0	
		Kola 11	-0.5	17.0	
4	East-central Finland	Porkkavaara	1.5	12.0	<i>Sarkkola et al.</i> [2009]
		Kangaslampi	1.5	15.0	
		Kangasvaara	1.5	13.0	
5	Northern-central Sweden	C6	1.7	9.7	<i>Ågren et al.</i> [2007]
		C9	1.7	10.8	
		C12	1.7	14.1	
		C14	1.7	11.9	
6	Central Ontario	Sörbäcken	1.5	18.0	<i>Laudon et al.</i> [2004] <i>Eimers et al.</i> [2008]
		HP3	4.8	8.5	
		HP3A	4.8	3.0	
		HP4	4.8	6.2	
		HP6	4.8	8.2	
		HP6A	4.8	12.0	
7	Southern Norway	PC1	4.8	15.2	<i>Strand et al.</i> [2008]
		Storgama 1	5.0	21.9	
		Storgama 2	5.0	13.0	
		Storgama 3	5.0	6.7	
		Storgama 4	5.0	9.1	
		Storgama 5	5.0	5.6	
		Storgama 6	5.0	10.1	
		Storgama 7	5.0	7.3	
		Storgama 8	5.0	11.0	
		Storgama 9	5.0	7.0	
		Storgama 11	5.0	13.6	
		Storgama 12	5.0	10.7	
8	Northwestern UK	Birkenes	6.0	5.5	<i>de Wit et al.</i> [2007] <i>Evans et al.</i> [2006]
		Allt na Coire nan Con	6.5	4.6	
		Dargall Lane	7.5	2.0	
9	Northeastern UK	Blue Lough	8.0	4.2	<i>Dawson et al.</i> [2011]
		Mar Lodge	7.0	4.0	
		Brundtland Burn	7.5	5.6	
10	Southern UK	Gaim	7.5	5.4	<i>Evans et al.</i> [2006]
		Muick	8.0	5.5	
		Feugh	8.5	6.9	
		Afon Hafren	9.0	2.4	
		Afon Gwy	9.0	2.4	
		Narrator Brook	10	1.8	

<sup>a</sup>Numbering corresponds to values in Figure 1.**Table 2.** Catchment Details of the North-Watch Sites

Catchment Name	Gauging Site	Abbreviation	Latitude/ Longitude	Area (km <sup>2</sup> )	Mean Elevation (m)	Relief (m)	Mean Annual Temperature (°C)	Mean Annual Precipitation (mm)	Mean Annual Runoff (mm)
Wolf Creek	Granger	Wol	62° 32'N, 135° 11'W	7.6	1700	750	-2.15	478	352
Krycklan	Svartberget	Kry	64°, 14'N, 19° 46'E	0.5	280	72	2.41	651	327
Sleepers River	W9	Sle	44° 29'N, 72° 9'W	0.41	604	167	4.66	1256	743
Mharcaidh	Site 1	Mha	45° 00'N, 75° 00'W	10	704	779	5.7	1222	873
Dorset	Harp 5	Dor	57° 6'N, 3° 50'W	1.9	373	93	4.94	980	577
Hubbard Brook	W6	Hub	43° 57'N, 71° 44'W	0.13	642	259	5.6	1423	917
Girnock	Littlemill	Gir	57° 2'N, 3° 06'W	30	405	620	6.73	1059	603
Strontian	Polloch	Str	56° 45'N, 5° 36'W	8	340	740	9.08	2632	2213
HJ Andrews	Mack Creek	Hja	44° 12'N, 122° 09'W	5.81	1200	860	9.22	2158	1744

**Table 3.** Summary of the Potential Explanatory Variables Tested Using the North-Watch Catchment Data<sup>a</sup>

	Average DOC	Residual DOC
Annual precipitation (P)	N.S.	N.S.
Annual runoff (Q)	N.S.	N.S.
Annual Evapotranspiration (ET)	N.S.	N.S.
Storage change (S) [Carey et al., 2010]	N.S.	N.S.
Runoff ratio (Q/P)	N.S.	N.S.
Wetland percentage	N.S.	N.S.
Relief/catchment area ratio	0.62**	0.32*
Elevation	N.S.	N.S.
Mean elevation above stream (MEAS, log values) [McGuire et al., 2005]	0.87***	0.53**
Mean distance from stream (along flow pathway) [McGuire et al., 2005]	0.52**	0.45**
Mean hillslope gradient to stream (along flow pathway) [McGuire et al., 2005]	0.55**	N.S.
Travel time proxy [McGuire et al., 2005]	N.S.	N.S.
Accumulated upslope area per unit contour length [Seibert and McGlynn, 2007]	N.S.	N.S.
Steepest gradient of the eight diagonal and cardinal directions	0.53**	N.S.
Steepest gradient with an infinite number of directions [Tarboton, 1997]	0.51**	N.S.
Downslope index [Hjerdt et al., 2004]	N.S.	N.S.
Topographic wetness index (TWI) [Seibert and McGlynn, 2007]	N.S.	N.S.
TWI combined with downslope index [Hjerdt et al., 2004]	N.S.	N.S.
Median subcatchment size [McGlynn et al., 2003]	N.S.	N.S.

<sup>a</sup>Adjusted  $r^2$  from linear regression of average DOC concentration and residual DOC concentration (from Figure 1) are provided. For spatially varying variables, such as elevation and several other topographic indices, catchment average values were computed based on the grid values. \* denotes significance at 90%, \*\* denotes significance at 95% and \*\*\* denotes significance at 99% confidential interval.

the surface waters draining the landscape also need to be incorporated into process-based models in order to simulate patterns of DOC accurately across space and time [Laudon et al., 2011].

[5] In order to test how the annual average DOC concentration is regulated across the mid- to high latitudes we used published literature values spanning a climatic gradient from  $-3^{\circ}\text{C}$  to  $+10^{\circ}\text{C}$  mean annual temperature (MAT). We assembled data from 49 non-wetland dominated catchments that were divided into 10 regional average values based on their geographic proximity. To provide the best possible integrative measure of stream concentration response to variable landscape features we focused on small to medium scale catchments. The regional annual average DOC concentration was compared to MAT for the region based on the most recent 30-year record. The regional MAT-DOC model was then tested on nine of the most well-investigated research catchments in the mid- to high latitude regions that are part of the North-Watch inter-comparison project [Carey et al., 2010; Kruitbos et al., 2012].

## 2. Methods

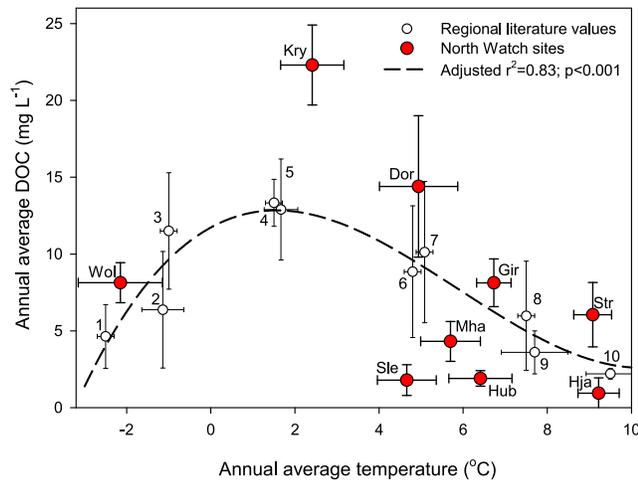
[6] Analyses of literature data were based on regional average DOC concentrations from largely unmanaged catchments with limited wetland cover (<20% of catchment area), using at least three independent streams for each region. Outliers, defined as sites deviating >75% from the average remaining value, were excluded to avoid biasing the results by extreme values. Only data from 1997 onwards were used to reflect contemporary conditions. As large rivers and lakes can both receive terrestrial (allochthonous) DOC and produce (autochthonous) DOC that can become incorporated in lake sediment or mineralized to  $\text{CO}_2$  during its residence time in surface water, we excluded catchments larger than  $1000\text{ km}^2$  and/or those with more than 1% lake area. In total, we assembled annual average concentrations from 49 catchments that were divided into 10 regional

averages (Table 1). The regional annual average DOC concentration was compared to long-term mean annual temperature data for the region using the most recent 30-year record from the respective national weather and/or climate agency. The more detailed data are derived from nine research catchments from Sweden, Scotland, Canada, and the USA that are all included in the North-Watch program [Carey et al., 2010] (Table 2).

[7] Topographic analysis of the North-Watch catchments was conducted based on 10 m Digital Terrain Models (DTMs) within the ArcMap Geographic Information System. A number of potential explanatory variables for the DOC concentration were computed and tested (see Table 3). For detailed description of the indices see references given in Table 3. As an indicator of drainage potential, the mean elevation above stream (MEAS) was defined as the elevation difference between a given location in the catchment and the point along the stream network at which water from this location enters the stream. The latter was determined by following the surface topography along the steepest gradient calculated based on high resolution gridded elevation data for each catchment. The MEAS was computed as the mean of grid cell values within the catchment. Any causal relationships were analyzed using regression analysis. Variables with non-normal distributions were log-transformed to achieve normality.

## 3. Results and Discussion

[8] We found that average DOC concentrations were strongly related to MAT across the regional catchment data derived from the literature. In general, the temperature dependence of DOC followed a third order polynomial with the highest concentrations in catchments with MAT between  $0^{\circ}$  to  $3^{\circ}\text{C}$ . We observed decreasing DOC concentrations at both higher and lower MAT (Figure 1). Furthermore, our results show that the deviation in DOC concentration of each of the individual North-Watch research catchments from this

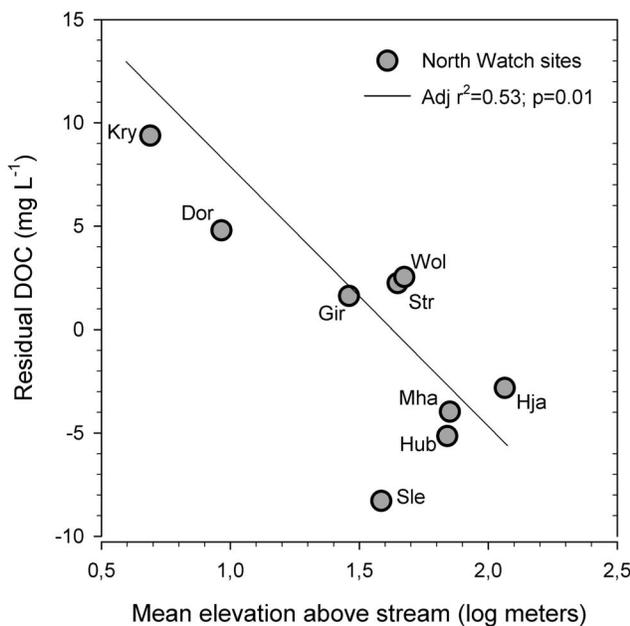


**Figure 1.** Cross-regional MAT (Mean Annual Temperature) - DOC concentration relationship. The regression line model ( $DOC = 11.62 + 1.51 \cdot MAT - 0.52 \cdot MAT^2 + 0.027 \cdot MAT^3$ ) is based on the literature data only (see Table 1 for details). Whiskers denote the range in MAT and annual average DOC concentrations for each of the regional average values. The North-Watch research catchments data (Table 2) are annual MAT and average DOC concentration at each site. Here whiskers denote standard deviation in annual DOC concentration and MAT.

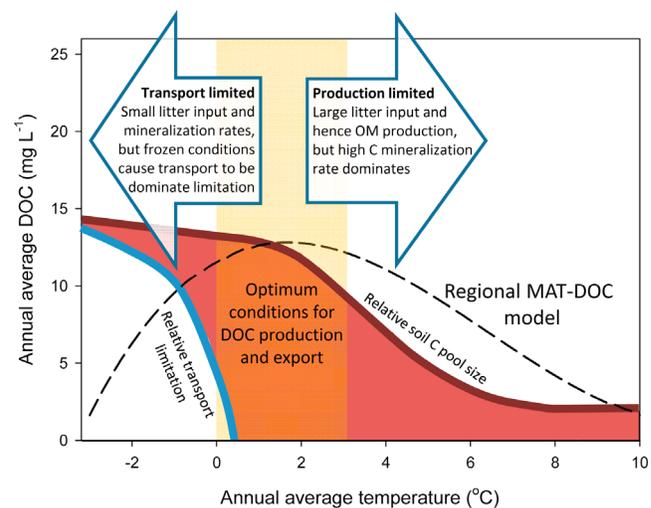
regional MAT-DOC model largely was accounted for by catchment topographic configuration (Figure 2). Specifically, over 50% of the deviation from the MAT-DOC model was explained by MEAS, which is an indicator of drainage potential.

[9] We hypothesize the physical controls of the observed regional DOC concentration maxima are a combination of relatively high production of litter, comparatively low degradation rates because of high lignin content from coniferous vegetation, and hydrological functioning. While NPP and hence litter production are mainly functions of the length of the growing season and climatic conditions, SOM mineralization rates are more directly temperature dependent and follow an exponential relation under optimal moisture conditions [Davidson and Janssens, 2006]. Our observed lower DOC concentrations in colder regions agree with results from a previous study in west Siberian wetlands spanning a temperature range from  $-8$  to  $+2$  C showing the highest DOC concentration in the uppermost temperature range [Frey and Smith, 2005]. The decline in DOC concentration in the warmer regions of our study ( $MAT > 3^{\circ}C$ ) was likely a consequence of higher mineralization rates. Others have found that mineralization increases more rapidly than NPP especially as vegetation becomes dominated by deciduous tree species whose litter is more readily decomposable [Hobbie et al., 2000]. This pattern is corroborated by  $^{14}C$  studies suggesting that soil carbon in temperate forests is mineralized, and hence recycled back to the atmosphere, more rapidly than soil carbon from the boreal forest [Trumbore, 2000].

[10] While water is a prerequisite for both the production and degradation of organic C, excessive water will result in water-logged, and hence anaerobic, conditions that slow mineralization processes. Although precipitation generally



**Figure 2.** Residual analyses of regional MAT-DOC model. Residual DOC concentration of the nine North-Watch sites vs. mean elevation above the stream (MEAS). The mean elevation above stream is the average elevation difference along the flow pathways from the catchment to the stream network and is a measure of the mean hillslope gradient towards the stream. The different sites are presented in Table 2.



**Figure 3.** Conceptual model of the regional MAT-DOC relationship from Figure 1 (hatched line) and the dominant environmental factors controlling the DOC concentration at higher (production limited) and lower MAT (transport limited). The relative available soil carbon pool is derived from data presented by Amundsen [2001], while the relative transport limitation is based on a conceptual understanding of the distribution of seasonal soil frost and permafrost and its role in water and DOC delivery to streams.

decreases towards higher latitudes, evapotranspiration rates decrease relatively more rapidly due to reduced energy for vaporization because of lower insolation [Kane and Yang, 2004]. Excess moisture conditions thus become more prominent with increasing latitude, reducing the mineralization rate even further. As a result, soil carbon content should increase with decreasing MAT if all other conditions remain constant [Amundsen, 2001] (Figure 3). However, in regions where MAT is below 0° C, permafrost becomes a limiting factor as water will be available but in a form that will not promote DOC production. Perhaps more importantly, frozen soils reduce the connectivity between organic soil sources and adjacent surface waters. This effect will be most prominent in areas of permafrost where only a small portion of the soil column is hydrologically activated during runoff events [Striegl et al., 2005; Frey and Smith, 2005]. A similar, but quantitatively less important effect on hydrological connectivity is caused by seasonal soil frost in the mid-latitude regions, whereby major SOM pools are bypassed during spring snow melt [Shanley et al., 2002; Laudon et al., 2007].

[11] Observed regional stream DOC concentration and forested SOM distribution paralleled MAT down to approximately 0°C. Below this temperature threshold, the regional MAT-DOC model predicted decreasing stream DOC concentrations. This is in contrast to many studies that have reported increasing SOM pools in northern systems [Dixon et al., 1994; Ping et al., 2008; Tarnocai et al., 2009]. Again, we hypothesize that this decoupling of the regional MAT-DOC model and SOM sources is caused by frozen conditions resulting in the dominant hydrological flow pathways bypassing frozen organic soils en route to the stream during large portions of the year.

[12] While the DOC concentration in streamflow on a regional scale appears closely coupled to MAT, large deviations from this model occur when considering individual catchments (Figure 1). This perhaps is not surprising given that the development of generalized models of catchment DOC patterns previously have been unsuccessful because of the uniqueness of each catchment system. Of all potential explanatory variables tested (Table 3), the correlation between MEAS and the MAT-DOC model residuals suggests that catchment topography has a strong influence on stream DOC concentrations in individual systems (Figure 2). The regional model tends to overpredict DOC concentrations in catchments with large elevation differences along the flowpaths while underpredicting in catchments with smaller differences. This pattern suggests that the availability of water not only regulates DOC concentration at the regional scale but also within individual catchments. We attribute this to slower water movement through low-relief catchments relative to steeper catchments where hydrological response to precipitation and snowmelt events is more rapid. This is consistent with water transit time analysis by McGuire et al. [2005] who showed strong topographic controls on transit time scaling relations. Similar to the global scale regulation of SOM [Amundsen, 2001; Post et al., 1982], more poorly drained soils lead to a larger build up of organic matter, especially in valley bottoms and riparian areas which are the landscape elements that are closest and most hydrologically connected to the stream. These also appear to be the areas that most effectively control stream DOC concentration [Bishop et al., 2004].

[13] We acknowledge the limitations of this meta-analysis approach, which is restricted by the available data provided in the cited literature (Table 1). As climate, vegetation, SOM pools, landforms and the hydrological functioning of each catchment have been co-evolving since the last glaciation, our analyses can merely indicate a strong physical connection between MAT, MEAS and DOC. To support (or reject) these findings, further work by others having access to long-term stream DOC records and high resolution DEM is needed.

[14] Northern regions contain large stores of organic carbon that represent on an areal basis nearly twice the amount of that observed in temperate forest regions [Tarnocai et al., 2009; Amundsen, 2001; Post et al., 1982]. While this disproportionately large soil carbon stock provides one of the most sensitive positive feedback scenarios for climatic warming [Gower et al., 2001], it is also a large potential pool for increasing C export via aquatic pathways [Frey and McClelland, 2009]. However, contrary to most previous reports, our simple regional MAT-DOC concentration model suggests that new long-term steady-state conditions will not necessarily always result in higher DOC concentrations in aquatic environments. Instead, the long-term trajectory of aquatic DOC concentrations may depend largely on the prevailing MAT. Warmer conditions in the mid- to high latitudes with MAT above 0°C will likely result in decreasing DOC concentrations in the future, whereas it is mainly regions that at present have a MAT below 0°C that are likely to experience increasing concentrations. Although transient changes may cause unexpected short-term results, the regional MAT-DOC model may lead the way to a more process-based understanding of the long-term trajectory of surface water DOC in a changing world.

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