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Linking carbon and sulphur cycling during simulated drought cycles in peat from six sites across the UK

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Summary

Water table draw-down is thought to increase peat decomposition and, therefore, DOC release. However, several studies have shown lower DOC concentrations during droughts relative to 'normal' periods with high water table. We carried out controlled incubation experiments at 10°C on 10x10 cm peat soil cores collected from six UK sites across a sulphur deposition gradient. Our aim was to quantify the balance between microbial consumption and chemical precipitation of DOC due to episodic acidification driven by sulphur redox reactions by comparing changes in soil water chemistry to microbial activity (i.e. soil respiration and trace gas fluxes). During dry periods, all sites showed a concurrent increase in SO_4 and soil respiration and a decline in DOC. However, the magnitude of change in both DOC and SO_4 varied considerably between sites according to historical sulphur deposition loads and the variation in acid/base chemistry.

Key index words: dissolved organic carbon; sulphate; drought; episodic acidification; microbial activity

Introduction

The impact of drought on dissolved organic carbon (DOC) dynamics in peat soils has been a topic of recent debate given widespread observations of increased DOC in freshwaters across Europe and North America (e.g. Worrall *et al.*, 2004). Reduced summer rainfall and increased temperatures should increase organic matter decomposition and DOC release. However, studies show conflicting results: some have observed DOC increases (Tipping *et al.*, 1999), others decreases (Pastor *et al.*, 2003), and some have seen no change at all (Blodau and Moore, 2003). Where DOC concentrations have declined during drought periods, explanations for the reduction in concentrations have also varied from physical changes in peat structure, to increased biological activity and microbial consumption of DOC, reduced biological activity and drought-induced acidification driven by sulphur redox reactions (Clark *et al.*, 2005; 2006).

Differing explanations for lower DOC concentrations during dry periods may in part be due to site specific characteristics. In particular, the relationship between sulphate (SO_4) and DOC may vary with the size of the sulphur pool (which that will be smaller at sites with lower sulphur deposition). To investigate the controls over DOC concentrations during dry periods on a regional basis, we carried out incubation experiments on peat soil cores collected from six UK sites across a sulphur deposition gradient. Our specific aims were to determine whether drying caused: (i) a reduction in DOC concentration; (ii) an increase in sulphate, soil water acidity and ionic strength; (iii) an increase in soil respiration (i.e. biological activity) whilst reducing anaerobic trace gas emissions; and (iv) the degree to which changes in DOC concentrations were due to biological consumption or chemical precipitation. Preliminary results for one week during the simulated dry period are presented in this paper.

Materials and methods

Eight peat cores (10 x 10 cm) were collected in PVC tubes from six UK sites across a sulphur deposition gradient between May-June 2006. Sites in order of high to low sulphur deposition are: River Etherow (ETH, South Pennines), Afon Gwy (GWY, Mid-Wales), Moor House (MH, North Pennines), Dargall Lane (DL, South-West Scotland), Loch Coire nan Arr (LCNA, North-West Scotland), Allt a'Mharcaidh (AM, Cairngorms). Mean total (marine and acid) sulphur deposition for these sites over the period of 1985-2005 was 57, 34, 31, 29, 26 and 10 kg S/ha/yr, respectively (Ron Smith, pers. comm.). More site information can be found at www.ukawmn.ucl.ac.uk and www.ecn.ac.uk.

Cores were placed into straight-sided Nalgene polycarbonate bottles (11 cm in diameter, 12 cm in length). Vegetation was removed prior to sampling. A 10 cm Eijkelkamp Rhizon SMS soil water sampler was inserted into each core. Cores were then slowly rewetted with deionized water until the surface peat was covered with 0.5-1 cm water, covered and placed in an incubator at 10°C for six months to allow soil water to stabilize, SO_4 to reduce and any labile carbon produced by decaying fresh roots to be consumed prior to the start of the experiment.

The experiment was in split into three stages: pre-treatment (all cores wet), 12 week drying treatment (4 cores dry, 4 cores wet for each site) and 20 week rewetting period (all cores wet). Soil cores were drained by pouring off excess water in the first instance (weeks 0 to 4) and further by extracting 20 mL every two weeks (weeks 4 to 12) using the Rhizon samplers. Cores were rewetted following soil water sample extraction on week 12 and monitored for a further 20 weeks. 20 mL of soil water was collected for analysis every four weeks using Rhizon SMS samplers following the procedure outlined in Clark *et al.* (2006). Samples were analysed for pH; conductivity; sulphate (SO_4), chloride (Cl) and nitrate (NO_3) by ion chromatography (Dionex); calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K) by atomic absorption spectrophotometry (Hitachi) and dissolved organic carbon (DOC) by combustion infra-red (Thermalox TOC-TN). Real-time trace gas flux measurements were taken before soil water sampling in weeks 0, 4, 8, 12, 16 and 32. We established a closed gas flow system by combining an INNOVA photoacoustic gas analyser (1412; LumaSense, DK) unit subsampling from a Li-Cor8100 (8100-102, Li-Cor Biosciences, USA) CO_2 analyser, its chamber placed above the soil core. This allowed simultaneous measurements of CO_2, CH_4 and N_2O fluxes (linear concentration increase over time) within a 10 min period per soil sample at a detection limit of less than 1 ppm. Only CO_2 and CH_4 data are presented in this paper.

Acid neutralizing capacity (ANC) was calculated in µeq/L as the difference between the sum of strong base cations (Ca, K, Mg, Na) and strong acid anions (Cl, NO_3, SO_4) as it represents a more conservative measure of acidity. Mean carbon fluxes for the dry period were calculated between week 4 and 8 by taking the mean of the trace gas fluxes measured in weeks 4 and 8 and the difference in DOC concentrations between week 4 and 8.

Results

DOC concentrations declined in dry soil cores at all sites, but with two distinct groups i.e. LCNA, DL, GWY and ETH (-74 to -86%) and MH and AM (-38 to -41%) (Fig. 1a). All dry soil cores also showed an increase in SO_4, corresponding to the site's sulphur deposition and therefore to the potential size of the soil sulphur pool (Fig. 1b). Acidity, presented as $[H^+]$ (Fig. 1c), also increased (i.e. pH declined) in the dry cores for all but the LCNA site, and was generally greater where SO_4 concentrations were highest. Increased acidity was accompanied by an increase in conductivity (as a measure of ionic strength) at four out of the six sites (Fig. 1d). The 'less polluted sites' in north-west Scotland (LCNA) and the Cairngorms (AM) both showed a decline in conductivity. ANC decreased at all sites and showed a very strong correlation with the change in DOC concentrations across all sites during week 8 (R^2 = 0.82, $p < 0.0001$, N = 48). Increases in NO_3 were also observed at LCNA, ETH and DL (3.2, 117 and 379 µeq/L, respectively).

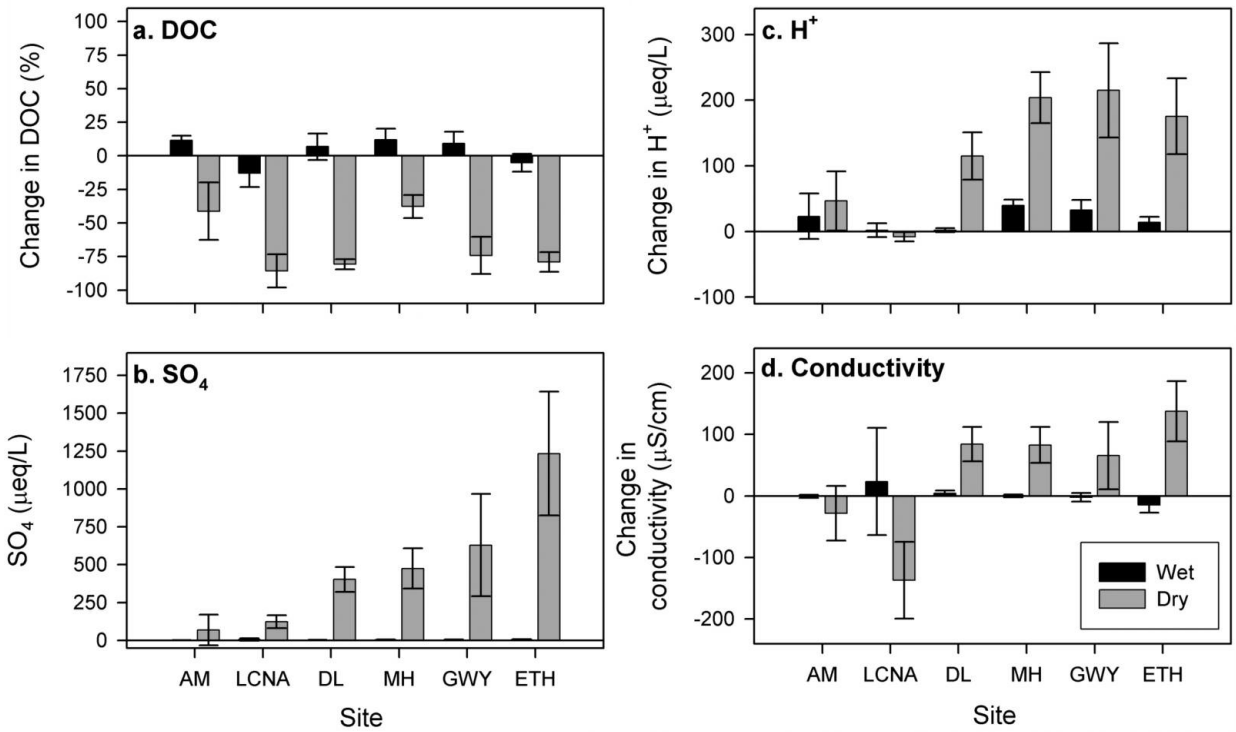

Figure 1. Change in soil water response in 'dry' period (week 8) from initial conditions (week 0). Mean values shown with standard deviation (N = 4). Site order from left to right is from the lowest to highest sulphur deposition.

Table 1. Mass balance for carbon fluxes in 'wet' and 'dry' treatments (week 8). Mean values shown (N = 4, except ETH 'dry' where N = 3).

Site	'Wet' treatment (μg C/g soil/day)				'Dry' treatment (μg C/g soil/day)			
	DOC	CO_2	CH_4	DOC:[CO_2 + CH_4]	DOC	CO_2	CH_4	DOC:[CO_2 + CH_4]
AM	0.71	39.5	2.94	0.01	-8.58	62.5	0.12	-0.14
LCNA	-4.42	52.7	3.63	0.05	-28.3	81.3	0.95	-0.35
DL	1.19	24.1	0.04	0.03	-19.9	47.0	0.07	-0.36
MH	1.35	22.4	0.15	0.08	-8.01	41.7	0.13	-0.20
GWY	0.31	36.8	2.09	0.004	-14.2	65.3	0.22	-0.22
ETH	-2.71	15.7	0.06	-0.13	-40.3	31.6	0.26	-1.32

Drying caused CO_2 fluxes to increase by around 50 to 100% and CH_4 fluxes to decrease (Table 1). However, there was no clear relationship between gas fluxes and sulphur deposition gradient. The ratio of the rate of DOC decline to total gas flux increased in the dry cores. Mass balance calculations showed that the rate of decline in soil water DOC was equivalent to around 14 to 36% of the total carbon gas flux during the dry weeks 4 to 8 at all sites except ETH, were the rate of decline in DOC was 32% greater than the total carbon gas flux (Table 1).

Discussion

Decreased DOC concentrations and increased SO_4, acidity and conductivity as observed by Clark *et al.* (2006) were seen at four out of the six sites. These sites were the most polluted with highest total sulphur deposition. One of the sites, MH, was the same as the site studied by Clark *et al.* (2006), showing these results were repeatable. As the data come from contained laboratory peat cores, changes in stream flow are not a plausible mechanism to explain an inverse relationship between SO_4 and DOC concentrations, as suggested by Eimers *et al.* (2008). Although two of the less polluted sites also did not show an increase in conductivity, with one showing no change in pH, all sites showed a decrease in the ANC and, therefore, evidence of drought-induced acidification. The degree of change in ANC depended not only on SO_4 but also on NO_3 concentrations and the amount of base cations available to neutralize the increase in acid anion concentrations. Although DOC suppression did not increase in line with SO_4 concentrations across the sites, even though a clear relationship was seen between change in SO_4 and DOC on a site-by-site basis (data not shown), a strong correlation between ANC and DOC was observed across sites. Therefore, variations in the acid/base status of soil water between sites can influence the degree to which drought-induced acidification affects DOC solubility.

Increased soil respiration during dry periods in all cores shows that biological activity increased in response to drying. This implies that DOC concentrations are unlikely to have declined because of reduced biological activity (i.e. DOC production) under dry/acidic conditions. Conversely, the amount of DOC possibly consumed and respired during microbial metabolism is uncertain but to be considered. Our mass balance calculations showed that it is theoretically possible for all of the DOC to have been consumed and respired at five out of the six sites only. However at ETH, the most polluted site, other processes such as chemical precipitation are required to explain the decline in DOC. The actual amount of DOC consumed will depend on its bioavailability. As DOC in peat tends to be highly refractory (Thurman, 1985), it is likely that only a small fraction was consumed with most CO_2 coming from decomposition of the bulk soil organic matter.

Preliminary data presented here provide evidence to support the hypothesis that reduced DOC concentrations during dry periods could be due to a combination of chemical precipitation and biological consumption. Data do not support the hypothesis that reduced DOC concentrations are due to a reduction in biological activity. However, further analysis considering changes in the chemical characteristics of DOC are required to correctly apportion the amount of DOC decline due to consumption and/or precipitation reactions. Correct apportioning of these factors is crucial in order to predict how DOC fluxes will respond to an increase in drought conditions as sulphur deposition across the UK continues to decline and water tables might change either due to management (e.g. blocking drains) or climatic changes (e.g. warming).

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