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Export of dissolved organic carbon and nitrate from grassland in winter using high temporal resolution, in situ UV sensing

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HIGHLIGHTS

- Grassland DOC/nitrate export data at high resolution by reagentless in-situ UV sensor.
- Rapid, transient but high impact perturbations of wintertime DOC and nitrate export.
- DOC export significantly higher than typical UK catchments; DOC correlated with nitrate, inversely correlated with pH and conductivity.
- DOC:NO_3-N ratios show microbial N assimilation not C limited, thus no high N export/ ecosystem N accumulation.
- A real time sensor enabling evaluation of climate change and land management strategies and a sentinel alarm.

GRAPHICAL ABSTRACT

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ABSTRACT

Co-deployment of two reagentless UV sensors for high temporal resolution (15 min) real time determination of wintertime DOC and nitrate-N export from a grassland lysimeter plot (North Wyke, Devon, UK) is reported. They showed rapid, transient but high impact perturbations of DOC (5.3–23 mg C L^{-1}) and nitrate–N export after storm/snow melt which discontinuous sampling would not have observed. During a winter freeze/thaw cycle, DOC export (1.25 kg C ha^{-1} d^{-1}) was significantly higher than typical UK catchment values (maximum 0.25 kg C ha d^{-1}) and historical North Wyke data (0.7 kg C ha^{-1} d^{-1}). DOC concentrations were inversely correlated with the key DOC physico-chemical drivers of pH (January $r = -0.65$), and conductivity (January $r = -0.64$). Nitrate–N export (0.8–1.5 mg N L^{-1}) was strongly correlated with DOC export ($r \geq 0.8$). The DOC:NO_3–N molar ratios showed that soil microbial N assimilation was not C limited and therefore high N accrual was not promoted in the River Taw, which is classified as a nitrate vulnerable zone (NVZ). The sensor was shown to be an effective sentinel device for identifying critical periods when rapid ecosystem N accumulation could be triggered by a shift in resource stoichiometry. It is therefore a useful tool to help evaluate land management strategies and impacts from climate change and intensive agriculture.

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1. Introduction

Dissolved organic matter (DOM) is one of the largest biologically active sources of carbon (C) and its transfer from terrestrial to aquatic environments is a fundamental component of the global biogeochemical cycling of carbon and other nutrient elements. DOM supplies energy to heterotrophic microbial communities that control key nutrient transformation processes, e.g. denitrification (Knowles, 1982), and helps control the availability of nutrients and trace metals for microorganisms and plants through the formation of complexes (Warnken et al., 2009).

There are environmental concerns regarding the transport of DOM from soil to water since it can lead to the export of species that can enhance eutrophication and cause pollution of receiving waters. Furthermore, DOM has been implicated in the transport of polycyclic aromatic hydrocarbons (Haftka et al., 2010), the mobilisation of some heavy metals (Fest et al., 2008) and nutrients such as phosphorus (Ros et al., 2010) and nitrogen. For example, nitrate accumulation in ecosystems is a key environmental issue and exhibits consistent and negative non-linear correlations with organic carbon availability along a hydrologic continuum from soils, through freshwater systems and coastal margins, to the open ocean (Taylor and Townsend, 2010). Dissolved organic carbon (DOC) is a major component of the DOM pool and its transfer from land to water constitutes a direct loss of carbon from soil systems, which has implications for both reserves of soil organic matter (SOM) and carbon sequestration. There have been significant increases in concentration levels of DOC in European and North American surface waters in recent decades (Clark et al., 2010). Hope et al. (1994, 1997) estimated that most UK catchments export between 10 and 100 kg C ha^{-1} yr^{-1} and Evans et al. (2006) reported that since 1998 there has been an average increase of 91% DOC in UK lakes and rivers. These increases have been attributed to climate change (Clark et al., 2010), rising levels of carbon dioxide leading to increased primary productivity and root exudation (Fenner et al., 2007; Freeman et al., 2004), the drying of the upland peat soils (Evans et al., 2006) and reduction in acid rain (Driscoll et al., 2003).

A better understanding of soil carbon turnover, storage and export, and the role of key physico-chemical parameters that control these processes, is essential to improve global carbon modelling and to inform policies that aim to sequester carbon (Dawson and Smith, 2007; Ostle et al., 2009). Reliable, high temporal resolution, high quality DOC measurements will provide data sets which will enable better pattern recognition and statistical interpretation of underlying (temporal) processes and drivers of DOC fluxes. Such data are needed to propagate C balance models in order to predict trends from different landscapes, land management strategies and climate change scenarios and UV sensing technologies have the capability of delivering such data (Sandford et al., 2010; Tipping et al., 2009). Losses of DOC from soils under different land use and management regimes have been reported, e.g. forests (Andreasson et al., 2009), uplands (Fiebig et al., 1990) and arable land (Mertens et al., 2007). However, despite the fact that grassland covers approximately 75% of UK agricultural land (Defra, 2009), few studies have investigated DOC losses from lowland temperate grassland (McTiernan et al., 2001; Boddy et al., 2007) and the impacts of land management and hydrology on the extent and patterns of short- and long-term DOC losses from these systems are largely unknown. Climate also impacts on carbon export and a recent study highlighted the effect of winter climate on the control of snowmelt DOC concentrations in northern latitudes with stream DOC concentrations in later seasons also affected by winter climatic conditions (Agren et al., 2010; Haei et al., 2010).

To improve prediction of carbon export to surface waters under differing land management and climate change scenarios it is necessary to obtain high temporal resolution, long term data to identify key, often rapid (1–2 h) changes in DOC export, especially from lowland temperate grasslands that dominate UK agricultural land. This paper reports the high temporal resolution (15 min), in situ, real time determination of DOC export from a hydrologically isolated, lowland permanent grassland lysimeter plot under little investigated winter freeze–thaw and precipitation conditions by the deployment (December 2009 and January 2010) of two reagentless in situ UV sensors in V-notch weirs accessing the two hydrological pathways (sub-lateral flow and drainage flow) draining a lysimeter plot.

2. Materials and methods

2.1. Site description

Rowden Drainage Experiment site, established in 1982 on previously unimproved, poorly drained pasture land on North Wyke Research farm, (Okehampton, Devon, SW England) is 180 m above sea level with a west to east ground slope of 5–10% and a mean annual rainfall of ~1100 mm. The soil is predominantly a clayey non-calcareous pelostagnogley of the Hallsworth series overlying the clay shales of the Crackington Formation (Dystric Gleysol of the FAO classification), and represents typical permanent grassland in the SW of England. The soil characteristics and hydraulic properties for the Hallsworth series are given in Table 1.

High annual rainfall coupled with a clay subsoil and <10 mm d^{-1} hydraulic conductivity, means that these type of undrained soils can become waterlogged. During such times, hydrological response to rainfall is very flashy with a large proportion of the response being saturation-excess overland flow (Armstrong and Garwood, 1991).

The Rowden Drainage Experiment consists of 12 lysimeter plots (1 ha each), in two blocks of 6. Each lysimeter plot is hydrologically isolated from its neighbour by gravel interceptors to isolate overland surface runoff and surface lateral flow to 30 cm. Half of the lysimeters, including plot 4 used in this study, are also drained to 85 cm by tile drains at 40 m intervals across the slope, overlain by mole drains at 2 m spacing and a depth of 55 cm down the slope (Armstrong and Garwood, 1991). Plot 4 had no inorganic fertiliser application but did receive dairy slurry inputs on 5th May and 7th October 2009, with application rates of ≈142 kg total N ha^{-1}.

2.2. Field drainage

The combined surface runoff and sub-lateral flow and the 85 cm field drainage waters (drainage flow) were collected in 1/2 90° V-notch weirs (BSI 1981). Precision Water Level Model 6541 sensors (Unidata, O'Connor, WA, Australia) in each weir measure the stage height changes for each hydrological pathway at 1 min intervals, the data being logged by a radio logger (CR215/CR216, Campbell

Table 1
Typical physical, chemical and hydraulic properties to a depth of 84 cm for the Hallsworth soil series. Adapted from Harrod (1981); n/a = not applicable.

Property	Horizon (cm) Apg (0–27)	Bg (27–66)	BCg1 (66–84)
% Sand			
(600 μm–2 mm)	1	2	7
(200–600 μm)	3	4	6
(60–200 μm)	8	8	8
% Silt (2–60 μm)	50	43	47
% Clay (<2 μm)	38	43	32
% Fine clay (<0.2 μm)	9	10	7
% Organic carbon	3.7	0.5	n/a
pH of soil (water extract)	5.3	6.0	6.1
Bulk density(g cm^{-3})	0.99	1.31	1.55
Water holding capacity (%)	51.3	45.7	33.3
Total pore space (% by volume)	63.3	50.4	41.5
Available water (% by volume)	22.1	16.6	14.7
Air capacity (% by volume)	12.0	4.8	8.2
Retained water (% by volume)	51.3	45.7	33.3