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Biodegradability of natural dissolved organic matter collected from a UK moorland stream

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ABSTRACT

The fate of dissolved organic matter (DOM) exported from headwaters is a large uncertainty in global carbon models and catchment biogeochemical process understanding. We examined the biodegradability of stream DOM collected during different flow conditions ($n = 12$) from a heather-dominated moorland headwater in NE Scotland. Freeze-dried DOM isolates were characterised, re-dissolved to 10 mg C L^{-1}, inoculated with indigenous stream sediment microbes and incubated, with and without added nutrients, to assess decomposition rates at different times up to 41 days. Biodegradable DOM ranged from 5.0 to 19% of the total transported DOM, representing 8.54 kg C ha^{-1} yr^{-1} (11.1% of the total DOC flux, calculated as 77.2 ± 39.0 kg C ha^{-1} yr^{-1}). No simple patterns with flow rate were apparent but accumulated antecedent rainfall, specific UV absorbance of DOM and ^{15}N content were significant predictors of the proportion of organic matter decomposed. In headwater streams draining organic-rich catchments, in-stream DOM decomposition processes act as a secondary control on the spatial variability of carbon species, and are important for establishing accuracy of aquatic carbon fluxes and cycling budgets. Moreover, biologically-mediated DOM decomposition represents a net 'climate forcing effect' via the soil–stream–atmosphere pathway, drives downstream ecosystem metabolism and should be incorporated in carbon predictive modelling and ecosystem process studies.

1. Introduction

Organic carbon (C) in streams is often transported in the form of dissolved organic matter (DOM), where it influences metabolism (through microbial processes), decreases water transparency and reduces the amount of sunlight for photosynthesis (Battin et al., 2008; Williamson et al., 2008). In upland headwaters, the dominant source of this organic C is from terrestrial stores. Any environmental change acting to destabilize the terrestrial C pool has ensuing implications for in-stream quality and hence biological processes (Billett et al., 2006).

It has been suggested that *ca.* 33% of global terrestrial organic C inputs to inland surface waters reach the oceanic sink and a minimum of 44% enters the atmosphere as gaseous carbon with the remaining 22% retained in sediments (Aufdenkampe et al., 2011). These estimates have an inherent uncertainty due to substantial spatio-temporal variability within and between ecosystems. This estimate is in approximate agreement with a modelled carbon budget for rivers in England and Wales of 10.3×10^6 g C km^{-2} yr^{-1} transported via rivers, with 4.2×10^6 g C km^{-2} yr^{-1} returned to the atmosphere (Worrall et al., 2007). In terms of DOC, recently modelled fluxes in UK rivers suggested that, at the tidal limit, between 70 and 78% of DOC released from terrestrial sources was potentially lost from across the catchment (Worrall et al., 2012). However, modelling soil water to tidal limit losses incorporates diverse

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carbon sources along the river continuum from a range of land uses and combines biotic and abiotic DOC losses using budget calculation approaches but fails to resolve in-stream processes.

Including aquatic C export components into terrestrial budgets has lead to the concept of the Net Ecosystem Carbon Balance (NECB) (Chapin et al., 2006). Aquatic C fluxes (particulate, dissolved and gaseous) have a pivotal influence on C budgets and cycling, determining whether the whole terrestrial system is a net source or sink of C (Billett et al., 2004; Dinsmore et al., 2010). Considering the NECB in terms of a GHG climatic forcing effect, (i.e. that an NECB ecosystem source is moving C from the terrestrial stores to the atmosphere), makes the assumption that aquatic C fluxes are processed in the streams, rivers and estuaries and outgassed as CO_2. In an extreme case, the C lost from the terrestrial stores is refractory and is all transported to the ocean to be buried in marine sediments then there is no net climatic forcing effect from aquatic C transfers. Whilst this extreme case seems unlikely, a source of uncertainty remains as to what extent of released C is 'bio-reactive' and undergoes biological decomposition, contributing to the return of C to the atmosphere. This dual role of aquatic pathways for DOC was conceptualised by Cole et al. (2007) as the 'active pipe' hypothesis, where inland waters are regarded as both reactors and conduits for terrestrial exports of C.

There is a substantial body of literature documenting studies of DOC concentration and fluxes. Research interest has been greatly stimulated in recent years by reports of increased DOC concentrations in surface waters in boreal regions of UK (average 91%), Scandinavia and USA over several decades (Evans et al., 2005; Monteith et al., 2007). Recently, there has been an important shift in focus for DOC research from consideration of amount of DOC to DOM composition and, in turn, the variation in its functional (bioavailability and reactivity) properties. Changes in DOM composition have been observed over event- (Hood et al., 2006; Stutter et al., 2007a), seasonal- (Stutter et al., 2007b) and decadal-timescales (Dawson et al., 2009). The controlling factors for these compositional changes may be altered interactions with podzol Fe sesquioxide surfaces, resulting from flow path changes; depositional changes affecting chemistry of these surfaces; changes in the extent of biological decomposition (Lumsdon et al., 2005a) or hydrological controls (Stutter et al., 2007a). Longer term shifts in the composition of DOM reaching rivers may be of profound future environmental significance affecting biogeochemical fate and reactivity.

In this context, the bioavailability and reactivity of natural organic matter in upland streams are under-developed areas of research. Examples of such work include the accessibility of river heterotrophic communities to the ecosystem energy supplied by terrestrial DOM (Battin et al., 2008) and organic matter associated with suspended particulate material (Dawson et al., 2012). DOM export (and associated inorganic nutrients) from different sources can control temporal variations of bacterial growth in receiving freshwaters. Changes in organic matter loadings caused by land use or environmental changes influence the metabolic balance of lakes and streams. Within a catchment in Sweden, drainage waters from a forested area supported higher bacterial production and growth efficiency than water derived from peaty mires. This bacterial production was fuelled by runoff contributions from the forested area during storm flows that comprised '*high quality*' organic C, whereas mire runoff, which dominated the stream inputs during lower flow periods, comprised '*low quality*' organic C and supported less bacterial production (Berggren et al., 2009). In these cases, *quality* has been used as a term for bioavailability and metabolic substrate utility to biota.

Thorp and Delong (2002) have suggested autochthonous carbon as the main driver of freshwater metabolism since 'allochthonous carbon is mostly recalcitrant'. In contrast, Del Giorgio and Pace (2008) showed the Hudson River acted as both a pipe (conveying >80% of the DOC to the ocean) and a reactor (where intense microbial activity acted mainly on particulate or allochthonous organic matter). Studies such as Cole et al. (2007) have been unable to discriminate between CO_2 efflux to the atmosphere from mineralization of organic matter sources within surface waters and the degassing of CO_2 derived from terrestrial sources. This highlights uncertainty in determining to what extent reactive organic matter, once exported from terrestrial stores has a climatic forcing effect by returning CO_2 to the atmosphere through biological in-stream processing. This study, utilising laboratory-based batch incubations, aims to determine factors that influence the extent and rate of decomposition of DOM isolated from a heather moorland headwater in the UK. Our hypothesis is that natural DOM in upland streams is not inert and is capable of undergoing decomposition to CO_2 by native communities. Furthermore, we propose that this degradation potential changes in time, related to the amount and characteristics of the DOM present, as conferred from simple compositional indicators.

2. Methods

2.1. Catchment characteristics

The area for this study was the headwaters of the Cairn Burn draining a 1.0 km^2 catchment on the SE fringe of the Grampian Mountains (57°N, 3°W), and is adjacent to the Glensaugh site of the UK Environmental Change Network (ECN) of similar altitude and soil type (http://www.ecn.ac.uk/sites/glens). Average annual rainfall was 1115 mm at 300 m during the study period (2004–2006). The catchment lies north of the Highland Boundary fault on coarse Dalradian acid schist drifts over the altitude range 250–455 m. The distribution of the catchment's soils (Strichen Association; Glentworth and Muir, 1963) comprises 40% Hill Peat (>50 cm organic horizon depth) on upper, gentle slopes covered by *Sphagnum* sp. and *Eriophorum vaginatum* (hair's-tail cottongrass). Peaty gleys comprise 14% by area. Peaty Podzols on intermediate slopes (average organic horizon depth 25 cm) have developed over 42% of the area on thin glacial till vegetated by *Calluna vulgaris* (heather), *Vaccinium myrtillus* (blaeberry), *Deschampsia flexuosa* (wavy hair-grass) and *Nardus stricta* (mat-grass). Freely drained humus–iron Podzols (3% of area; average organic horizons depth 15 cm) occupy steeper slopes covered by *C. vulgaris* and *V. myrtillus*. Land use is limited to rough sheep grazing

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