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High fluvial export of dissolved organic nitrogen from a peatland catchment with elevated inorganic nitrogen deposition

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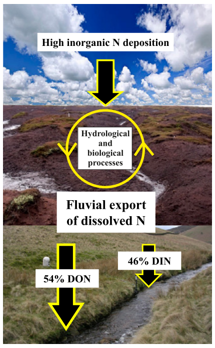
HIGHLIGHTS

- DON is a significant component of TDN in an acidified peatland fluvial system.
- DON and DOC are closely coupled under different flow and seasonal conditions.
- In contrast to DON, there are no marked seasonal variations in DIN concentration.
- DIN concentrations in the catchment waters are high.
- Despite decades of high N deposition the peatland catchment remains a sink of N.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates seasonal concentrations and fluxes of nitrogen (N) species under stormflow and baseflow conditions in the peat dominated Kinder River catchment, south Pennines, UK. This upland region has experienced decades of high atmospheric inorganic N deposition. Water samples were collected fortnightly over one year, in combination with high resolution stormflow sampling and discharge monitoring. The results reveal that dissolved organic nitrogen (DON) constitutes ~54% of the estimated annual total dissolved nitrogen (TDN) flux (14.3 kg N ha^{-1} yr^{-1}). DON cycling in the catchment is influenced by hydrological and biological controls, with greater concentrations under summer stormflow conditions. Dissolved organic carbon (DOC) and DON are closely coupled, with positive correlations observed during spring, summer and autumn stormflow conditions. A low annual mean DOC:DON ratio (<25) and elevated dissolved inorganic N concentrations (up to 63 μmol l^{-1} in summer) suggest that the Kinder catchment is at an advanced stage of N saturation. This study reveals that DON is a significant component of TDN in peatland fluvial systems that receive high atmospheric inputs of inorganic N.

1. Introduction

Nitrogen (N) is the limiting nutrient of primary production in most ecosystems (Vitousek and Howarth, 1991; Howarth and Marino, 2006) and rarely exceeds 0.5 mg N L^{-1} in undisturbed upland catchments (Reynolds and Edwards, 1995). However, there has been increasing evidence that atmospheric deposition of N alters the balance between the retention capacity of soils, biotic cycling and catchment losses, leading to significant impacts on freshwater ecosystems through eutrophication and/or acidification (Allott et al., 1995; Evans et al., 2000; Curtis et al., 2005; Helliwell et al., 2007a; Gruber and Galloway,

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2008; Dise et al., 2011; Durand et al., 2011). A number of studies have investigated total N flux in catchments (e.g., Allott et al., 1995; Robson and Neal, 1997; Evans et al., 2000; Curtis et al., 2004, 2005; Helliwell et al., 2007a, 2007b), but many have focused on dissolved inorganic nitrogen (DIN = NO_3–N plus nitrite (NO_2–N) plus ammonium (NH_4–N)), to the near exclusion of dissolved organic nitrogen (DON). Although reactive, and perhaps the most significant with respect to water quality, DIN represents only a portion of the total dissolved nitrogen (TDN) flux. In temperate uplands where peat soils dominate (Adamson et al., 1998; Chapman et al., 2001a), and in streams draining both disturbed and undisturbed watersheds (Campbell et al., 2000; Willett et al., 2004; Brookshire et al., 2005; Martinelli et al., 2010; Vogt et al., 2013), DON can contribute substantially to TDN.

The inadequate characterisation of DON as a component of TDN has led to a limited understanding of its dynamics in upland fluvial systems. This dearth of knowledge is highlighted by the omission of organic N in major water monitoring programmes of the UK in particular and Europe in general. However, since the late 1990s, there has been recognition of the potential significance of DON in the TDN flux of upland regions (Adamson et al., 1998; Chapman and Edwards, 2001; Chapman et al., 2001a; Clark et al., 2004; Cundill et al., 2007; Helliwell et al., 2007a, 2007b; Vogt et al., 2013). Most UK studies have focused on the uplands of SW England, Scotland, Wales and the North Pennines. On average, DON accounted for more than 40% of the TDN flux in these upland regions (Reynolds and Edwards, 1995; Adamson et al., 1998; Chapman et al., 2001a; Chapman and Edwards, 2001). However, knowledge of DON is still limited in systems receiving high levels of inorganic N deposition.

Several studies have shown that an initial increase in inorganic N deposition leads to an increase in carbon (C) storage through assimilation by vegetation or storage in soil organic matter (SOM) (Holland et al., 1997; Rowe et al., 2006; Evans et al., 2006a). But, if a sustained increase in inorganic N deposition is not accompanied by an increase in reactive C, the soil C/N ratio will decline, resulting in an increase in N concentration in soil solution, and subsequent leaching to the aquatic environment, including freshwaters (Holland et al., 1997; Goodale et al., 2000; Rowe et al., 2006). A change in the winter–summer seasonal pattern of DIN concentration is a signal of N saturation and leaching in upland streams and rivers (Helliwell et al., 2007a). In unperturbed upland environments, DIN concentration will be low in summer when biological uptake exceeds supply of N from atmospheric deposition, mineralisation and nitrification (Reynolds and Edwards, 1995). Contrastingly, with an increase in atmospheric deposition of N and a decline in biological uptake in winter, higher DIN concentrations in soil solution and stream water are often observed (Reynolds and Edwards, 1995). This seasonal pattern is climate driven, with temperature and moisture playing crucial roles (Birch, 1960; Reynolds et al., 1992; Monteith et al., 2000). The winter–summer seasonal patterns of DON tend to exhibit more variability between regions (Chapman et al., 2001a; Clark et al., 2004; Helliwell et al., 2007a). For example, in the Scottish uplands, Chapman et al. (2001a) observed higher DON concentration in summer than in winter (with some variations in the ratio of seasonal mean concentration between regions), but Clark et al. (2004) found no consistent seasonal DON trend at their sites in Scotland. Similar variability in DON was observed in south Pennines sites (Helliwell et al., 2007a). This variation reflects broad differences in catchment characteristics, including soil type, vegetation coverage and the soil C–N pools (Chapman et al., 2001a; Helliwell et al., 2007a).

Although DIN is expected to constitute a greater proportion of TDN in areas with long-term high atmospheric inorganic N deposition (Allott et al., 1995), the relative importance of organic N accumulation in peat-dominated ecosystems may vary along a deposition gradient, depending on direct biomass uptake of atmospheric N, and the rate of litter decomposition (Yesmin et al., 1995). Over a period of time, high atmospheric inorganic N deposition may alter the soil microbial processing of organic matter (OM) and/or the availability of organic substrates that lead to DON/dissolved organic carbon (DOC) formation, resulting in marked losses of DON/DOC to the fluvial environment (Pregitzer et al., 2004), especially under storm conditions (Clark et al., 2007; Inamdar and Mitchell, 2007). Whilst there are indications that concentrations and/or composition of N species and DOC could vary under different flow conditions and environments (Buffam et al., 2001; Williams et al., 2001; Inamdar and Mitchell, 2006, 2007; Neff et al., 2013), significant gaps in our understanding of the temporal dynamics and transport mechanism of these nutrients, particularly in peatland systems, remain (Clark et al., 2007). The rapid shifts in stream flow during storm events, and the significant heterogeneity in the hydro-chemical characteristics of upland catchments (Shand et al., 2005), suggest that routine spot sampling which is widely used for flux calculation in upland systems may not accurately estimate solute or nutrient fluxes, particularly if storms are under-represented (Clark et al., 2007; Rothwell et al., 2007). This study was undertaken to provide a better understanding of the dynamics of dissolved N species and C in peatland systems with a history of high atmospheric N deposition. We conducted an intensive hydro-chemical monitoring of TDN [DIN + DON] and DOC during stormflow and baseflow conditions in an acid-impacted peat-dominated catchment of the south Pennines, UK. To our knowledge, this study represents the first investigation into the annual stormflow and baseflow dynamics of TDN [DIN + DON] and DOC in this upland region. We address four key research questions.

1. Do the patterns of DIN and DON differ under baseflow and stormflow conditions? And does temperature, as a proxy for biological activity, influence this pattern?
2. What are the seasonal patterns in N species and DOC concentration?
3. How significant is DON in the TDN flux?
4. What is the relationship between N species and DOC?

2. Study area

This study was conducted in the Kinder River catchment covering an area of 394 ha in the Dark Peak area of the south Pennines (Fig. 1). The south Pennines has a history of high atmospheric inorganic N deposition, with current levels at ~28 kg N ha^{-1} yr^{-1} (Helliwell et al., 2007b). Rainfall for the study catchment is 1157 mm, whilst average annual air and water temperature is 8.5 °C and 7.9 °C, respectively (Dec 2012–Nov 2013). The vegetation of the catchment is dominated by *Eriophorum* spp. (Cotton grass), *Vaccinium myrtillus* (Bilberry) and *Empetrum nigrum* (Crowberry). Although low-density sheep grazing occurs within the catchment, land is generally managed to ensure the provision of high water quality. Land management practices typically entails the protection of watercourses, stabilisation of soils, and moorland restoration aimed at reducing organic, particulate and nutrient losses into the fluvial environment (United Utilities, 2011). The soil of the catchment is mainly blanket bog (52%) and shallow peaty soils (34%) over grit and coarse sandstone. Approximately 43% (1.82 km) of the Kinder River drains Kinder Scout; a grit stone plateau which is overlain by thick deposits (2 to 4 m depth) of blanket bog incised by erosional gullies. Varying degrees of degradation including vegetation loss, widespread gullying, high sediment and DOC losses, etc. (Evans et al., 2005, 2006; Rothwell et al., 2008a; Allott et al., 2009; Shuttleworth et al., 2014), have been reported in the headwaters of the Kinder plateau. Approximately 22% of the Kinder plateau (United Utilities, 2011) and ~13% (52 ha) of the Kinder River catchment is bare and eroding peat. The Moors for the Future Partnership is currently undertaking a work to restore the ecological integrity of degraded areas of the Kinder plateau. To this end, 173 ha of the Kinder River catchment headwater have undergone some restoration (between 2010 and 2013), including gully blocking, liming, fertilizer — N (Nitrogen) P (Phosphorus) K (Potassium) application for seeding, and heather brash spreading. In June/July of the hydrological period under investigation (Dec 2012–Nov 2013), ~138 ha of the catchment headwater was limed [$CaCO_3$