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Groundwater nitrogen composition and transformation within a moorland catchment, mid-Wales

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ABSTRACT

The importance of upland groundwater systems in providing a medium for nitrogen transformations and processes along flow paths is investigated within the Afon Gwy moorland catchment, Plynlimon, mid-Wales. Dissolved organic nitrogen (DON) was found to be the most abundant form of dissolved nitrogen (N) in most soils and groundwaters, accounting for between 47 and 72% of total dissolved nitrogen in shallow groundwater samples and up to 80% in deeper groundwaters. Groundwater DON may also be an important source of bio-available N in surface waters and marine systems fed by upland catchments. A conceptual model of N processes is proposed based on a detailed study along a transect of nested boreholes and soil suction samplers within the interfluve zone. Shallow groundwater N speciation reflects the soilwater N speciation implying a rapid transport mechanism and good connectivity between the soil and groundwater systems. Median nitrate concentrations were an order of magnitude lower within the soil zone (<5–31 μg/L) than in the shallow groundwaters (86–746 μg/L). Given the rapid hydrostatic response of the groundwater level within the soil zone, the shallow groundwater system is both a source and sink for dissolved N. Results from dissolved N_2O, N_2/Ar ratios and dissolved N chemistry suggests that microbial N transformations (denitrification and nitrification) may play an important role in controlling the spatial variation in soil and groundwater N speciation. Reducing conditions within the groundwater and saturated soils of the wet-flush zones on the lower hillslopes, a result of relatively impermeable drift deposits, are also important in controlling N speciation and transformation processes.

1. Introduction

Many upland catchments in the UK are acidic and sensitive to acid loading due largely to the presence of poorly buffering bedrock such as shales and granites (Edmunds and Kinniburgh, 1986). Emissions of SO_x, NO_x and ammonium, account for the acid loading to these catchments, and although SO_x emissions are declining owing to legislative changes the relative importance of nitrogen emissions has increased (Skeffington, 2002). The detrimental effects of nitrogen deposition on surface water chemistry have been widely reported both in Europe and North America (Wright et al., 2001; Stoddard, 1994), however, recent improvements caused by emission targets have occurred (Skjelkvale et al., 2005). While most studies have focussed on the effect of dissolved inorganic nitrogen (DIN) in terms of nitrogen cycling and water quality, the role of dissolved organic nitrogen (DON) in nitrogen cycling and bioavailability has also been shown to be

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important in a range of environments (Scott et al., 2007; Seitzinger et al., 2005; Jones et al., 2004; Willett et al., 2004; Seitzinger and Sanders, 1997; Carlsson and Graneli, 1993).

Studies in the Plynlimon catchments of mid-Wales have provided long-term records of changes in stream nitrogen chemistry and have enabled the impact of changes in historical deposition and landuse to be assessed (Neal et al., 1997a; Reynolds et al., 1997, 1992). Simplistic models, which consider the groundwater system as an impermeable compartment, fail to model changes in stream chemistry successfully and the need to understand and include processes within the groundwater system is clear (Neal et al., 1997b, 1988). Most studies in the Plynlimon catchments that have included groundwater chemistry have been limited to the forested Hafren catchments of the river Severn and the effects of felling on nitrogen breakthrough (Neal et al., 2003; Hill and Neal, 1997; Neal et al., 1997c) and catchment scale heterogeneity (Shand et al., 2005).

The importance of the groundwater system in these upland catchments has been highlighted by a number of studies. Stable isotopes of Sr, O and H have been used to show that pre-event groundwater dominates stream flow generation during storm episodes in the forested catchment, and that the flow path for rainfall is via fracture flow rather than flow-through the soil zone (Shand et al., 2007; Neal and Rosier, 1990). O and H stable isotopes have also shown that soil pipeflow during storm events in the Gwy catchment has a significant proportion of pre-event water (Sklash et al., 1996). Groundwater is an important source of base cations in soil pipeflow during storm events, and may lead to an increase in stream base cation concentrations (Chapman et al., 1997). Baseflow chemistry has been recognised as more alkaline than soilwater chemistry and this is attributed to a groundwater compartment (Neal et al., 1997a). Conservative solutes (e.g. Cl) in streams display strongly damped responses relative to rainfall implying that there is considerable storage within the system and that the groundwater component of storm hydrographs must be significant (Kirchner et al., 2001; Neal and Rosier, 1990; Reynolds and Pomeroy, 1988). Changes in piezometric heads in the shallow groundwater system and the interconnection between the groundwater, soilwater and overland flow in response to rainfall events have shown the dynamic nature of water movement (Haria and Shand, 2006, 2004).

Examination of DIN run-off fluxes (1995–1997) within the Gwy catchment showed that the outputs were 7% of inputs, accounted for entirely by nitrate, and the catchment has been classified as a net immobiliser of inorganic nitrogen (Curtis, 2002). Topographic controls on nitrate leaching from soils in the Gwy catchment have been proposed within a conceptual model to explain the spatial variability of nitrate in grassland catchments (Evans et al., 2004). Soils on the upper hill slopes (>10°) within close proximity of the stream network (<10 m) are considered 'nitrate leaching zones' which input nitrate (NO_3) to the stream network. Extensive deep peat areas export DON but are proposed as effective barriers to inorganic nitrogen transport (Evans et al., 2004).

DON is an important soluble N pool within the soil system but its role in soil N cycling is still poorly understood (Jones et al., 2004). Clark et al. (2004) found that ammonium (NH_4) leaching appeared to be influenced by soil type, climate and landuse, and DON decreased with increasing elevation. Recent research has highlighted the role of groundwater systems in providing a locally important function in nitrogen transformations and processes along flow paths, and much of this work focused within the riparian zone (Maitre et al., 2003; Sanchez-Perez et al., 2003). Catchment scale factors, such as vegetation cover and geology, have also been found to influence N speciation and concentration in an upland blanket peat catchment (Cundill et al., 2007, Helliwell et al., 2007). The role of the groundwater system within the hydrology and N cycling of the Gwy catchment has been largely ignored. Hydrochemical processes in upland systems are characterised by high spatial heterogeneity making assessments of N-saturation based on single point stream data problematic (Cundill et al., 2007; Shand et al., 2005; Chapman et al., 2001). Understanding the catchment scale controls on these processes is key to assessing N-saturation.

Denitrification is a microbially mediated process in which oxidised nitrogen species (i.e. NO_3 or nitrite (NO_2)) are reduced under anaerobic conditions to N_2, provided there is a source of organic carbon (Knowles, 1982; Payne, 1973). This process also produces intermediate reduced species; NO_2, nitric oxide (NO) and nitrous oxide (N_2O). N_2O may also be produced as a result of nitrification (microbial oxidation of ammonium to nitrite and nitrate) although this process may not be significant in the peaty soils and saturated wet-flush zones given the anaerobic conditions and high organic carbon pool (Machefert et al., 2002). Microbial denitrification can be an important process in the soil compartment, where conditions are suitable, such as soil moisture, pH and temperature (Schipper et al., 1993). It can also take place within the aquifer system, and N_2/Ar ratios and N_2O may be used as indicators of denitrification at depth within groundwaters in anaerobic environments (Blicher-Mathiesen et al., 1998; Wilson et al., 1990; Vogel et al., 1981). Denitrification in riparian areas is an important mechanism in reducing nitrate loading to surface water (Maitre et al., 2003; Burt et al., 1999). Riparian zones are important regulators of nitrate and denitrification may be a significant process for nitrate removal within the groundwater systems of the Gwy catchment.

Coupling groundwater level data, chemistry from the soil and groundwater compartments and a basic understanding of the hydrogeological controls will enable the development of a simple conceptual model of groundwater flow and nitrogen processes in the shallow groundwater system within the interfluve and riparian zones. In this paper the dissolved nitrogen chemistry (both DON and DIN) and dissolved gases of the groundwater system of the Gwy catchment are investigated, both temporally and spatially, in the context of the soil and rainfall chemistry, and the significance of DON discussed in terms of nitrogen cycling within the catchment. Groundwater and soilwater data presented are compared with the spatial conceptual model for nitrogen leaching proposed by Evans et al. (2004).

2. Study area

2.1. Site description and landuse

The Gwy catchment is situated on the east side of the Plynlimon study area, 25 km from the west coast of Wales and lying within the headwaters of the river Wye (Fig. 1). The