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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. A significant correlation between dissolved organic carbon (DOC) and DON in the shallow groundwater system suggests that during the autumn and winter months the flux of DON from the soil zone may be regulated by the wetting up and release of soil organic matter. DON needs to be taken into account when considering catchment N balances otherwise N export from upland catchments could be significantly underestimated. 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 soil N speciation implying a rapid transport mechanism and good connectivity between the soil and groundwater systems. Median dissolved inorganic N concentrations were an order of magnitude lower within the soil zone (10-25 mg/L-N) than in the shallow groundwaters (100-750 mg/L-N). 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 N2O, N2/Ar ratios and dissolved N chemistry suggests that microbial N transformations (denitrification) 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.

Groundwater nitrogen transformations 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. A significant correlation between dissolved organic carbon (DOC) and DON in the shallow groundwater system suggests that during the autumn and winter months the flux of DON from the soil zone may be regulated by the wetting up and release of soil organic matter. DON needs to be taken into account when considering catchment N balances otherwise N export from upland catchments could be significantly underestimated. 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 soil N speciation implying a rapid transport mechanism and good connectivity between the soil and groundwater systems. Median dissolved inorganic N concentrations were an order of magnitude lower within the soil zone ($10–25\,\mu g/L$-N) than in the

shallow groundwaters (100–750 µg/L-N). 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) 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.

Keywords: DON; Groundwater; Denitrification; Nitrification; Upland Catchments

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, and to a lesser extent 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 (Evans and Monteith, 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 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., 1997c). 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; Neal et al., 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) 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). Baseflow chemistry has been recognised as more alkaline than soil water 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). 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). Changes in piezometric heads in the shallow groundwater system and the interconnection between the groundwater, soil water and overland flow in response to rainfall events have shown the dynamic nature of water movement (Haria and Shand, 2006; Haria and Shand, 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 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 (>10º) within close proximity of the stream network (<10m) 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.

The role of DON in soil N cycling is still poorly understood but is an important soluble N pool within the soil system (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). 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 the paper the dissolved nitrogen chemistry (both DON and DIN) and dissolved gases of the groundwater system of the Gwy catchment is 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, 25km from the west coast of Wales and lying within the headwaters of the river Wye (Figure 1). The catchment area is 4 km^2 and comprises rough grazing for sheep. Grazing density is approximately 2.5 ewes ha^{-1}. The altitude range for the catchment is 380–730 m above sea level. Sample sites are shown in Figure 1. The study area has undergone relatively few landuse changes and no historical grassland improvement, and therefore may also provide an important baseline assessment of the effects of N inputs from precipitation on groundwater nitrogen dynamics for this area and other upland catchments in the UK.

2.2   Rainfall and hydrology

Mean annual precipitation is approximately 2500 mm and annual streamflow is of the order of 2000 mm although there is significant inter-annual variability (Kirby et al., 1991). There is greater than average precipitation and flow in the period September–March and less than average April–August. Actual evaporation is estimated to be 15–17% of precipitation. Hydrograph separation estimates the baseflow index (proportion of stored water) for the Gwy is 0.34 (Kirby et al., 1991). Groundwater levels in these upland areas, previously considered to be 'impermeable' beneath the soil zone, also show rapid responses to precipitation events, highlighting the importance of groundwater compartments in within-catchment water transport (Haria and Shand, 2006; Haria and Shand, 2004; Shand et al., 2001). Rainfall and stream flow data are shown in Figure 2 for the period May 2003 to May 2004. The streams shows characteristic flashy responses to precipitation events with lag times between rainfall events and stream flow of the order of hours, although this is dependent on antecedent conditions. During the sampling in February 2004 the reach adjacent to the transect was in flood and extensive overland flow and pipe-flow were observed.

2.3   Soils and vegetation

The soil types vary across the catchment: stagnopodsols and peat are found on the upper hillslopes, peat in the wetlands which dominate the topographic hollows, and gleys in the valley bottom. Soils on the upper slopes are thin (often <0.5 m). In the wetland hollows the peat soils have deeper profiles (>0.6 m). In the mid 1970s, lower parts of the Gwy moorland catchment (down stream of the study site) were subject to pasture improvement schemes by heavy additions of fertiliser and lime, a process which has historically led to enhanced nutrient losses (Roberts et al., 1986). The catchment has a complex network of soil pipes which play an important role in the rapid routing of water to the network of streams. Macroporous or bypass flow from the soil zone to the shallow groundwater system is thought to be an important transport mechanism

within the catchment (Evans et al., 2004). Acid grasses *Nardus-Festuca,* dominate vegetation on the hillslopes, and *Juncus*, *Molinia* and *Sphagnum* dominate the wetland peat areas.

2.4 Geology and hydrogeology

Figure 1 shows the simplified geology of the Gwy catchment. The bedrock geology of the Gwy catchment consists of Upper Ordovician and Silurian shales, blue-grey mudstones and grits. Drift deposits are derived locally and consist of boulder clay found generally at the base of the hill slopes. These deposits are associated with the wetland areas and provide a relatively impermeable barrier on which deep peaty soils can form. Colluvium is widespread on the higher slopes (Bell, 1972) The bedrock is weathered and highly fractured within the weathered zone, the top 4–8 m. Below this the bedrock is increasingly competent although a complex facture network still exists. It is proposed that the driving head for the regional groundwater flow is from the upper slopes toward the valley bottom (Shand et al., 2005). Observations in the adjacent Hafren forested catchment show that the response in piezometric heads to precipitation events is very rapid and implies rapid recharge via fracture and bypass flow (Haria and Shand, 2004; Shand et al., 2004). Haria and Shand (2004) observed piezometers with artesian flow in the valley bottom and on the lower slopes indicating upward heads close to the river in the Hafren, a forested catchment of the river Severn. Given the fractured nature of the catchment and the steep topography a binary mixing model is proposed for the shallow groundwater system between recent recharge and older, deeper groundwaters.

3 Materials and methods

3.1 Instrumentation

The site infrastructure comprised a transect of four nested piezometer sites (GW-A to D) and five other piezometer nests at different locations in the Gwy catchment, a total of 19 piezometers. Each piezometer was sealed using expandable foam in order to sample specific groundwater horizons. Stream samples were taken at two locations, at a site on a first order tributary of the

Afon-Gwy, the Nant Cerrig, and at another site in the middle reaches of the Afon-Gwy adjacent to the boreholes in the riparian zone (see Figure 1). Soil water (sampled over the same time period as the groundwater) was also sampled from a series of soil suction sampling nests located along the transect SW-A to D, adjacent to the piezometer nests. A composite rainfall sample from two open collectors, one from the Gwy catchment and one from the adjacent Hafren catchment, was used for the rainfall chemistry (the rainfall chemistry from the two sites does not differ significantly (Kirby et al., 1991)). Table 1 gives a detailed breakdown of the sample sites included in this study.

3.2 Sampling and analysis

Four-weekly samples were collected from the piezometers and streams between April 2003 and April 2004, two-weekly samples were taken from the soil suction samplers over the same period. Weekly rainfall subsamples were collected over the same period. Field measurements of dissolved oxygen (DO), pH, specific electrical conductance (SEC) and Eh (redox potential) were measured using a flow-through cell. Owing to the reducing conditions (Eh ~0–200 mV) and relatively low storage coefficient of the shale, stable Eh readings were not obtained during pumping in several boreholes, and Eh results are not reported. Groundwater samples were taken using a 12-V submersible pump, piezometers were purged (typically 2–3 volumes) and samples were taken only when stable field measurements were obtained. Groundwater, soilwater, streamwater and rainfall samples were filtered using 0.45 μm cellulose filters into sterile containers and stored refrigerated in the dark. These samples were analysed for TON (NO_3-N and NO_2-N), NO_2-N and NH_4–N using colorimetric methods. An aliquot of the filtered sample was acidified (1%v/v nitric acid) for trace metal determination by ICP-MS. A subsample of groundwater and streamwater was filtered using a silver 0.45 μm filter and stored in chromic-acid-washed glass bottles. These were analysed for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) using a C/N analyser. Soilwater samples were stored in sterile brown glass bottles. DON was calculated by subtracting the DIN (TON+ NH_4–N) from TDN.

Dissolved gasses were sampled from only a small selection of piezometers using evacuated glass bulbs and analysed for N_2O by gas chromatography, and N_2 and Ar by mass spectrometry based on the method of Martin et al. (1995).

4   Results

4.1   Temporal changes in groundwater levels

Groundwater responses from three shallow piezometers in the highly fractured part of the shale, GW-A1, C1 and D1, are shown in Figures 3a for the period June 2003-May 2004. Figure 3b shows the responses in three deeper piezometers GW-A2, B2 and C2 over the same time period, in the competent shale which can be described as having a more discrete network of fractures. Groundwater heads were measured monthly and all results are expressed as metres below ground level (mbgl), results from artesian piezometers were set to zero. Heads in the deeper piezometers were almost always higher than those in the shallow, indicating an upward hydraulic potential and confining conditions at depth. All the piezometers showed a high degree of variation in head with time. The degree of variation was similar for the shallow piezometers GW-A1 and C1 (range: 0.2–1mbgl), located close to the river and in the wet flush zone of the interfluve, and greater in GW-D1 (range 0–1.7mbgl), located further up slope. Responses in the intermediate piezometers showed similar variations for all three locations and trends were similar for the shallow and the intermediate piezometers. Haria and Shand (2004) showed that groundwater levels respond in a consistent way at different depths in the adjacent Hafren forested catchment and explained this in terms of a hydrostatic response to rapid recharge from rainfall upslope. It appears that a similar mechanism may be in operation within the moorland catchment.

4.2   Spatial variations in rainfall, soil water, groundwater and streamwater chemistry

Median concentrations of N-species and DOC in rainfall, soil and groundwater chemistry, are shown in Table 2. In the rainfall inorganic nitrogen species dominate with approximately equivalent median concentrations of NO_3-N and NH_4-N, 173 and 199 µg/L respectively, DON

accounts for only 19% of TDN with a median concentration of 87 µg/L. The different soils showed similar results for all sites with DON being the dominant species (91–95%). Inorganic N concentrations were low (<5–20 µg/L), and at all sites median soil TON (largely NO_3-N) concentrations were equivalent or higher than NH_4-N, with the highest median TON concentrations found on the upper slopes at site D. The groundwater sampled from the shallow piezometers had higher concentrations of inorganic N than soilwaters, with the proportion of DON generally being lower than that found in soils. The proportions of inorganic N varied from site to site and were in contrast to the more uniform proportions in rainfall and soilwater. Median NO_2-N concentrations were above the detection limit in half of the shallow sites. In all but two sites, DON was the dominant form of dissolved nitrogen in the groundwaters (range 47–98% TDN), at most sites it accounted for >70% TDN. Deeper piezometers also show inorganic N concentrations greater than those found in soils, but considerably less than those in the shallow piezometers. NH_4-N is the dominant inorganic N species in deeper piezometers, with GW-I2 being the notable exception. Pipe flow data shown are from two separate storm events; in both cases TON is the dominant form of inorganic N, and DON accounted for around 70% of TDN. The two stream sites had different N chemistry, while TON is the dominant inorganic species and DON the dominant form of dissolved N for both, the median TON concentration in the Cerrig is twice that found in the Gwy. Conversely, the median DON concentration in the Gwy is twice that found in the Cerrig. DOC concentrations are generally highest in the soil samples (4.0–5.9 mg/L) and show relatively little variability. Concentrations are lowest in the deeper groundwaters (0.4–3.2 mg/L) showing more variability and are intermediate in the shallow groundwaters. The obvious exception to this general trend is GW-H which has the highest concentrations found at any site and higher concentration in the deeper piezometer.

4.3   Temporal changes in groundwater and streamwater chemistry

While some sites showed consistent temporal trends over the study period, many are characterised by a high degree of variability both within and between sites. The low sampling

frequency (monthly) makes detailed assessment of short-term changes difficult (Kirchner et al., 2004), especially in such responsive catchments where antecedent conditions are critical. Nevertheless, they are useful for indicating potential seasonal change (especially in groundwaters which have generally longer residence times). These were investigated in more detail within the detailed transect (sites A-D).

Temporal changes in four dissolved nitrogen species (DON, TON, NO_2-N and NH_4-N) for the shallow groundwaters between June 2003 and May 2004 are shown in Figure 4, and changes in DON, TON, DOC and NH_4-N in the streams over the same time period are shown in Figure 5. Trends in DON show some consistency for the eight shallow piezometers but have a high degree of temporal variability; the highest concentrations for most sites were detected in the summer and winter months, while the lowest concentrations were found in spring and autumn. Concentrations of inorganic N show a high degree of variability both within and between sites. At several sites and on more than one occasion neither TON or NH_4-N were detected in the shallow groundwaters. Site GW-G on the upper hill slope was unusual in that it showed a clear increasing trend in TON over the sampling period. NO_2-N also showed a variable temporal trend and was only detected in the sites that were in the wet flush zones on the hill slopes and in the riparian zone adjacent to the Gwy.

All the N species also showed a high degree of temporal variability for the stream sites (Figure 5). Temporal trends for DON and TON were similar for both the Cerrig and the Gwy, with higher DON concentrations in the Cerrig possibly due to the abundance of peat in the catchment of the upper Cerrig. Temporal trends in streams were also similar to those observed in the shallow groundwaters with DON concentrations highest in the summer and winter months. NH_4-N concentrations were low for both the Cerrig and the Gwy and were close to or below the detection limit, making it difficult to assess temporal trends. However, highest concentrations for the Cerrig were found in the summer months and highest concentrations for the Gwy were found in the winter months. TON was detected in both streams throughout the sampling period, and while trends were similar for both streams concentrations in the spring and summer months were

significantly lower for the Gwy than the Cerrig (reflected in the median concentrations, Table 2). Comparable concentrations were found in both streams in the winter and spring months, and were also the highest during this period. DOC concentrations showed a higher degree of variability and were highest in the summer and autumn and lowest in the winter and spring, contrasting with the results for TON.

4.4   Dissolved gases and nitrite in groundwater

Table 3 shows the results for dissolved N_2O and N_2/Ar in groundwaters. In January 2004 all but two sites the N_2O concentrations were below detection limit. The highest concentration was found in the shallow groundwater at site GW-G1, in the upper hill slope (56.7 µg/L), and 8.7 µg/L was detected on the upper blanket peat, site GW-I2. Further sampling for N_2O in March 2004 found significantly higher concentrations at two sites, GW-A2 and GW-B1, and N_2O was also detected at GW-C. N2O concentrations increased with depth and down the transect flow path. These results show that there is a high degree of spatial and season variation in dissolved gases. Four N_2/Ar results were measured and of these, three are well in excess of the atmospheric equilibrated ratio of ~40 (allowing for a excess-air component), indicating that denitrification is taking place. One is close to the equilibrium ratio, implying that denitrification is not significant in this case. Sites that showed significant excess of N_2 were GW-A2, GW-C1 and GW-C3 within the wetland and riparian zone. Nitrite can also be an indicator of denitrification, being an intermediate (meta-stable) species in the aerobic denitrification of NO_3-N. Nitrite was detected in significant concentrations in shallow groundwaters within the wet-flush zone and in the riparian zone close to the Gwy, and there is a general trend in increased nitrite concentrations down the transect GW-D to GW-A towards the river, in the direction of groundwater flow (Table 2). This is also the case on the opposite side of the Gwy at sites GW-E to GW-G. This suggests that the potential for denitrification within the shallow groundwater system and soil increases down the flow path and that there may be local geochemical and hydrological factors that are controlling nitrogen transformations. The relatively high N_2O concentrations found at GW-G is more likely

to be an indicator of microbial nitrification, since it contains predominantly oxidised nitrogen species.

4.5   *Changes in nitrogen chemistry with depth*

Figure 6 shows TON, NH_4-N, DON, DOC, Fe and DO as a function of depth for all the groundwater results. DIN species (TON and NH_4-N)show a general decrease in concentration with depth, as does DOC and DO. In contrast, DON shows little variation with depth as a whole. Overall, Fe concentrations also decrease with depth, with highest concentrations (*ca*. 5 mg/L) in the shallow groundwaters. While the trends shown in Figure 6 give an overview of the geochemistry of the shallow groundwater system, they hide the processes that are occurring along potential flow paths. Median concentrations of TON, NH4-N, DON, Fe and DOC/DON ratios are shown as a function of depth for three nested piezometers within the transect GW-A to GW-D in Figure 7, where A is closest to the Gwy. The main changes in nitrogen chemistry within the interfluve are as follows: for TON and NH_4–N the highest concentrations are in the shallow groundwaters, *ca*. 3–5m deep, and the profiles can be characterised as bell shaped; TON (largely NO_3-N) concentrations decrease down transect (in direction of local groundwater flow) towards the Gwy stream; NH_4-N concentrations display the opposite trend and increase along transect towards the river; there is a clear change in N speciation down the transect but no net change in DIN; DON shows no clear change with depth or direction of groundwater flow; DOC/DON ratios decrease with depth at all sites, but nests GW-C and GW-D in the wetland and riparian zone show the highest ratios within the shallow groundwaters <1 m deep. The Fe profiles show a small increase in concentration in the intermediate depth samples at site D. At site C and A there is a large increase in Fe concentration with depth within the shallow groundwater system and then a decrease in the deeper piezometers, and overall greater Fe concentrations within the soil zone. These results show that there is a redox interface along the shallow groundwater flow path with relatively oxic conditions in the groundwaters of the upper slopes and reducing groundwater conditions in the wet-flush and riparian zones. The changes in

redox conditions within the shallow groundwaters may be important in controlling N speciation and might explain some of the spatial heterogeneity within the catchment. The decrease in Fe concentrations in the deeper groundwater samples is probably due to the higher pH with depth and the lower available Fe in the less weathered bedrock.

5 Discussion

5.1 Spatial and temporal variations in nitrogen chemistry

The catchment can be described as N limited as evidenced by the soil N chemistry. The inorganic N species are present in low concentrations relative to the inputs from rainfall —this is the case across the catchment (in various sub-catchment settings) and does not show any significant seasonal variation. However, soil N speciation did vary between sites: on the upper slopes nitrate was present in higher concentrations relative to soils on the lower slopes including in the peaty soils of the wet flush zones and soils adjacent to the Gwy. This observation is also supported by the relatively high nitrate concentrations found in the Cerrig, an upstream tributary of the Gwy, and corroborates the conceptual model of nitrate leaching zones proposed by Evans et al. (2004). This is in contrast with DON where concentrations were significantly higher in the soil zone across the catchment than in atmospheric inputs, and did not vary significantly between different soil types either. The N chemistry of the shallow groundwater system reflects the N chemistry of the soil zone in terms of N speciation, however, significantly higher inorganic-N concentrations were found in the groundwaters relative to the soil waters. This suggests that leaching from the soil zone is taking place either through incomplete immobilisation or leaching of inorganic N, or by rapid macropore flow. Groundwater fluctuations within the transect took place within 0–1mbgl, responding rapidly to recharge events. Soil N could also be flushed into the shallow groundwater system owing to changing water levels. As the groundwater levels rise in response to recharge, a front of leached dissolved N could be picked up from the soil zone.

There is a high degree of temporal variation in dissolved N within the groundwaters and surface waters, low concentrations also made assessing temporal trends difficult for some N species.

Seasonal trends in DIN were highly site specific, and were likely controlled by a number of site-specific factors including soil microbial activity (nitrification and denitrification), fluctuations in groundwater levels, geological controls on drainage and permeability and redox conditions within the groundwater system. The large proportion of DON at most sites controlled seasonal changes in TDN. The DON/DIN ratio increases significantly with depth within the soil and groundwater system (Figure 8) and may be explained in terms of increased residence times e.g. a decrease in modern atmospheric sources of DIN from a few decades ago (<30–40 years) or microbial transformations of DIN (e.g. denitrification of DIN). Previous studies in temperate forested catchments in south America, where anthropogenic inputs are very low, have shown a relatively high proportion of DON in streams (Perakis and Hedin, 2002). DON has also been found to be an abundant form of dissolved N in streams across a range of catchments in the US (Scott et al., 2007). This study has shown DON it to be the most abundant form of dissolved N in groundwaters and streams in an upland moorland catchment of relatively low permeability with comparatively high depositional sources of anthropogenic N. DON concentrations in the shallow groundwater system showed similar seasonal trends to those in the Gwy and the Cerrig. Figure 9 shows a scatter plot of DON and DOC for shallow groundwaters during autumn and winter. It can be seen that there is a significant positive correlation (r^2=0.56, p>0.01) between the two variables during this period, while the correlation in the spring and summer is very poor (data not shown, r^2= 0.002, p>0.01). This implies that the flux of DON from the soil zone is regulated by the wetting up and release of soil organic matter during the autumn and winter months (see Figure 2 for precipitation and flow data). While the spatial and seasonal variations appear to be site-specific, more general trends have emerged across the catchment due to underlying geological, hydrologic and geochemical controls which may apply to other catchments.

5.2 N transformations within the soil and groundwater system

A preliminary conceptual model has been proposed (Figure 10) based on the detailed study along the transect of nested boreholes and soil suction samplers within the interfluve zone of the Gwy

catchment. This model is consistent with other parts of the catchment with similar geological controls in explaining the spatial variability in dissolved N. Dissolved inorganic N speciation was also found to vary with depth and with changing redox conditions, implying that N transformations are taking place within the soil and shallow groundwater system (Figure 10). Excess dissolved N_2 found within groundwater in the wet-flush and riparian zones show that denitrification is an important N transformation process beneath, as well as within the soil zone. Reducing conditions exist within the shallow groundwaters beneath the wet flush and riparian zones; this factor and the plentiful supply of DOC also mean that microbial denitrification is possible. Denitrification could account for the reduced nitrate concentrations in the shallow groundwater system within the wet-flush zone, and along the flow path within the riparian zone; increases in nitrite concentrations down flow also corroborate the suggestion of microbial denitrification as an important N transformation process.

Microbial nitrification is also an important transformation process under acidic soil conditions and in riparian environments (Matheson et al., 2004). Soil pH within the transect is acidic (range 4.6–5.7) and the underlying shallow groundwaters were also acidic (<6.0). At some locations, e.g. sites B and C, in the wet flush zone the soil was saturated for some of the year; at site A the soil is more freely draining owing to the underlying geology and superficial deposits. There is potential for nitrification within the freely draining acidic soils on the upper slopes and this could explain the predominance of nitrate in the soils and shallow groundwaters, and streams on the upper slopes relative to other locations. The highest dissolved N_2O concentration was found at GW-G1, also on the upper reaches and the site with the highest median TON concentrations. This suggests that nitrification is taking place and may also help to explain why so many sites had low N_2O concentrations in terms of being limited by absolute DIN concentrations. The higher concentrations found in March compared to January show that there is a high degree of temporal variability in dissolved gases, and may suggest lower microbial activity, and hence lower denitrification/nitrification potential, within the shallow groundwater in winter months.

These results support the proposed nitrate leaching zones on the upper slopes and the role of the wet-flush zones as barriers to nitrate leaching (Evans et al., 2004).

The groundwater DON concentrations were comparable with soil concentrations and did not change significantly between sites or with depth, suggesting that DON behaves in a conservative way within the groundwater system. DON was found to be the most abundant form of dissolved N in most soils and groundwaters, accounting for 47–72% total dissolved nitrogen in shallow groundwater samples in the transect and up to 80% in deeper groundwaters. In shallow groundwaters located on the upper blanket peats DON accounted for up to 75% TDN. While the absolute concentrations of DON do not seem to change significantly with depth in the soil and shallow groundwater system, there is an overall decrease in DOC/DON ratio (Figure 7). The overall loss of DOC with depth (Figure 6) along with a decrease in DOC/DON (Figure 7) ratio suggests that microbes are using DOC as a source of C. Considering DIN inputs and outputs alone underestimates the overall N cycling within the catchment and may also underestimate the biologically-available N within the streams, rivers and estuaries fed by upland surface and groundwaters. While N uptake/loss is an important process in the soil and groundwater, TON concentrations are too low in the soils to explain the stream TON. This implies that much of the stream export of TON is from the shallow bedrock groundwater system, and that by-pass macropore flow is an important mechanism in the transport of oxidised N from upland catchments.

6 Conclusions

Within the Gwy catchment, groundwater N transformations are important in modifying N speciation and N export from upland catchments. The key findings from this moorland catchment study are as follows: (i) DON was found to be the most abundant form of dissolved N in most soils and groundwaters, accounting for 47–72% total dissolved nitrogen in shallow groundwater samples in the transect and up to 80% in deeper groundwaters; (ii) the significant correlation of DOC and DON in the shallow groundwater system suggests that the flux of DON

from the soil zone may be regulated by the wetting up and release of soil organic matter during the autumn and winter months; (iii) Median dissolved inorganic N concentrations were an order of magnitude lower within the soil zone (10–25 μg/L-N) than in the shallow groundwaters (100–750 μg/L-N); given the dynamic nature of the groundwater table in the soil zone this highlights the important role of the shallow groundwater system as both a source and sink for dissolved N in upland catchments; (iv) shallow groundwater N chemistry reflects the soil N chemistry implying a rapid transport mechanism between the soil and shallow groundwater systems; macro-porous flow and rapidly responding groundwater levels within the soil zone are proposed as mechanisms for N transport to depth within the groundwater system; (v) the increase in DON/DIN and decrease in DOC/DON with depth suggest that microbial activity and the mixing of groundwater of varying ages within the groundwater system plays an important role in controlling the concentration and spatial variation in N speciation in the soil and groundwater system on a catchment scale; (vi) redox conditions within the groundwater and saturated soils of the wet-flush zones are important in controlling N speciation and are a result of the relatively impermeable drift deposits and soils which underlie this study area, and other similar upland catchments.

DON needs to be taken into account when considering catchment N balances, otherwise N export from moorland catchments could be significantly underestimated. DON may be an important source of bio-available N in surface waters, estuarine and marine systems fed by upland catchments, and could have wider implications in terms of regulating microbial biomass production and eutrophication within fresh water and marine systems.

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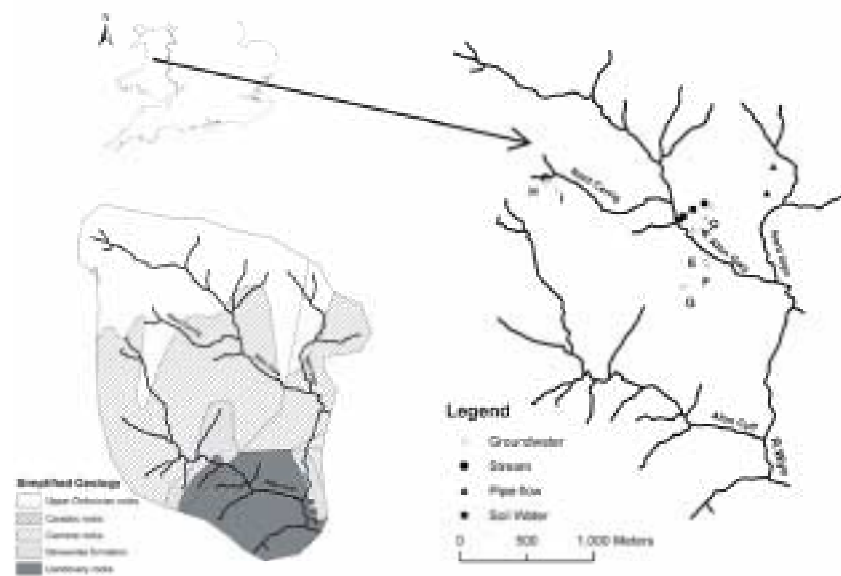Figure 1. Location of study area, sample sites and catchment geology
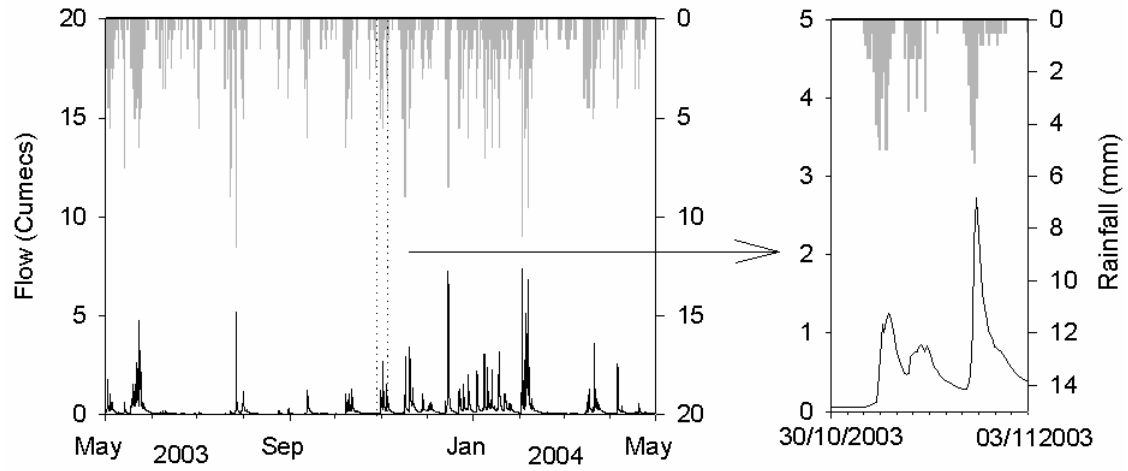
Figure 2. Rainfall and river flow

Figure 3. Changes in piezometric heads in a) shallow groundwaters b) deeper groundwaters
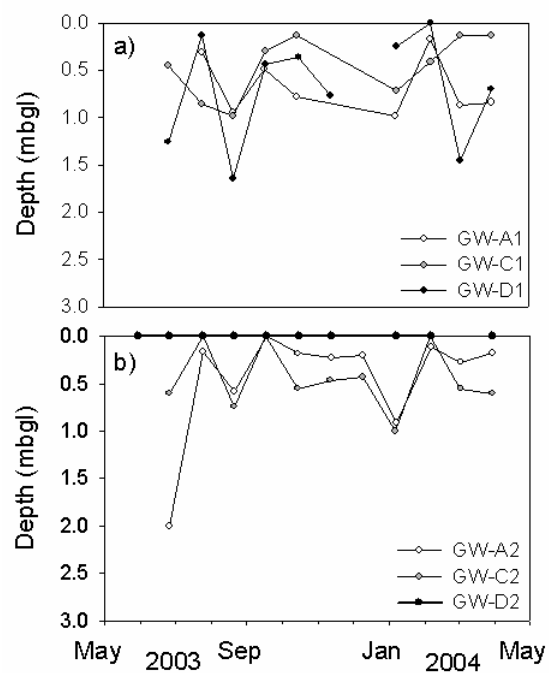
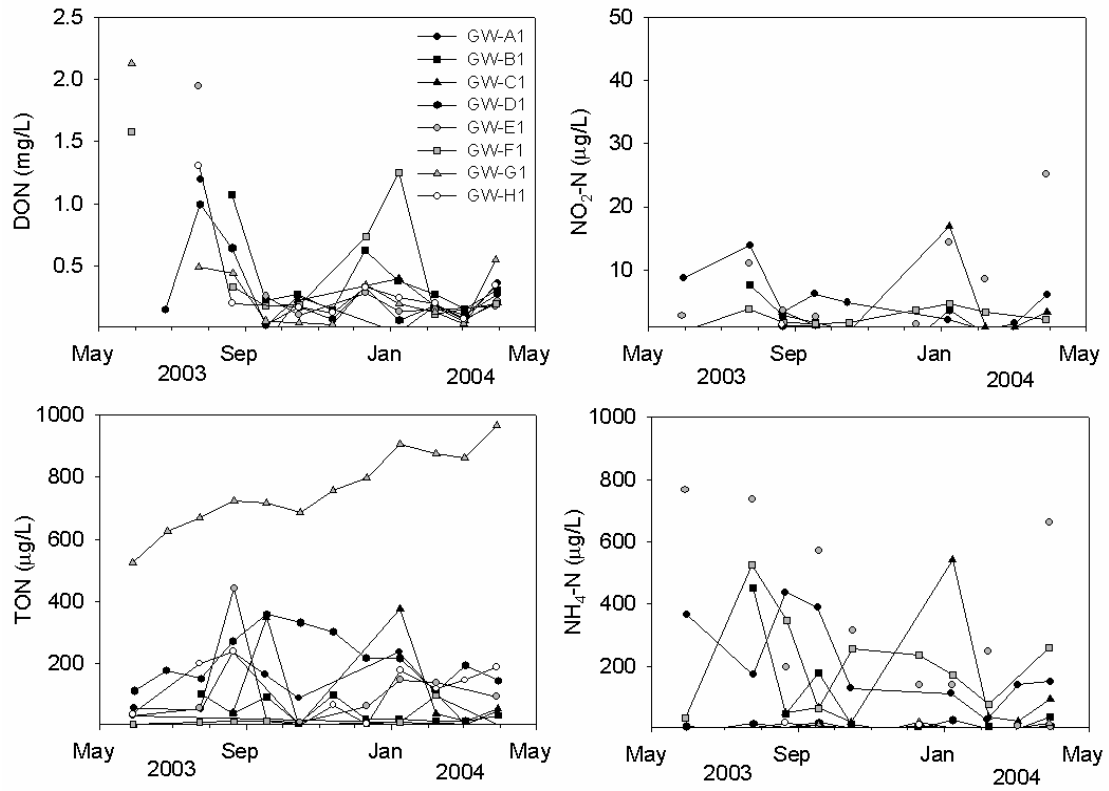Figure 4. Temporal changes in shallow groundwater N chemistry
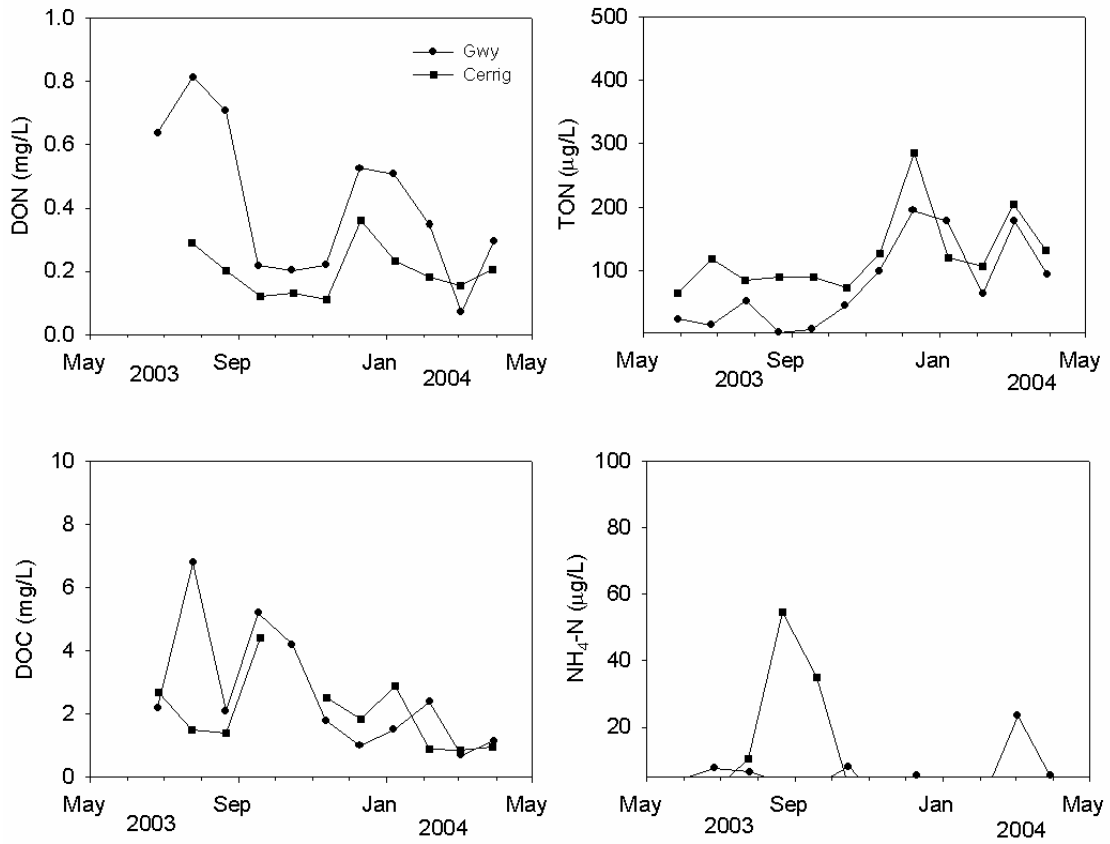
Figure 5. Temporal changes in stream chemistry

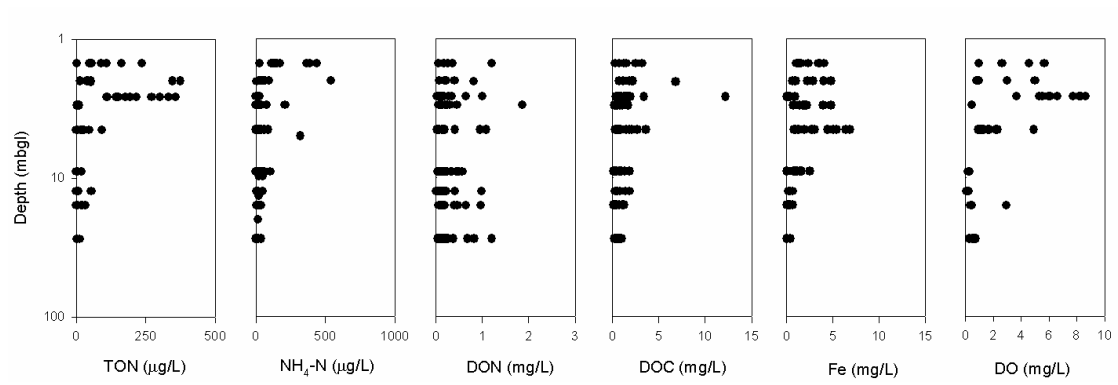Figure 6. Changes in groundwater chemistry with depth

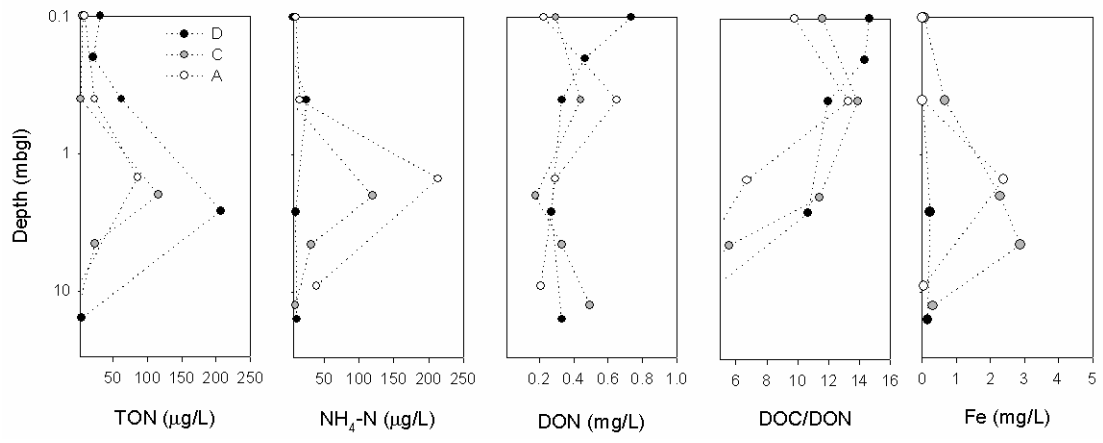Figure 7. Changes in soil and groundwater chemistry within the transect

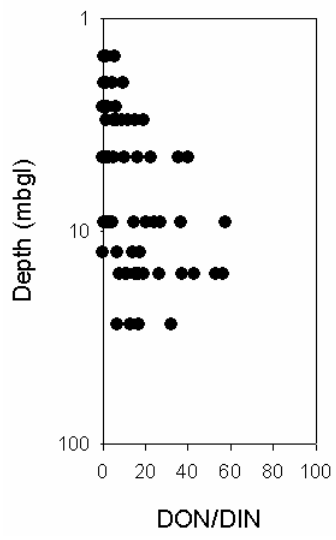Figure 8. Changes in groundwater DON/DIN with depth

Figure 9. Scatter plot of DOC vs DON in shallow groundwaters (October 2003-March 2004)
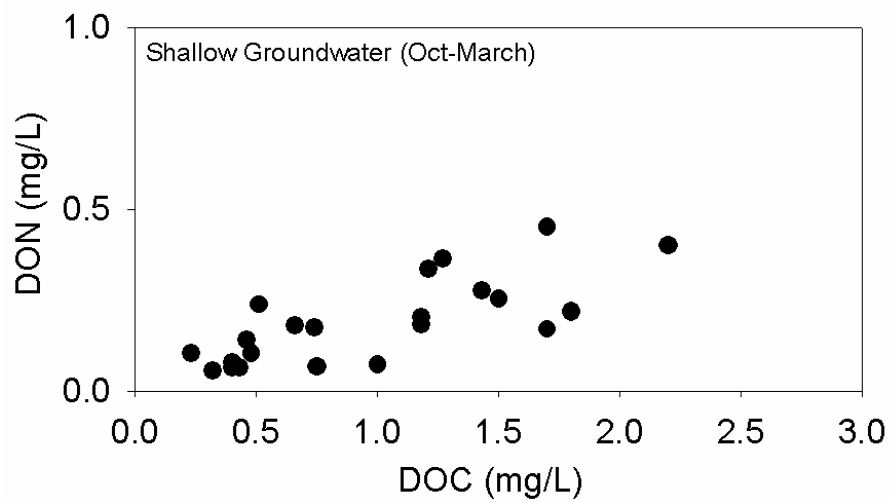
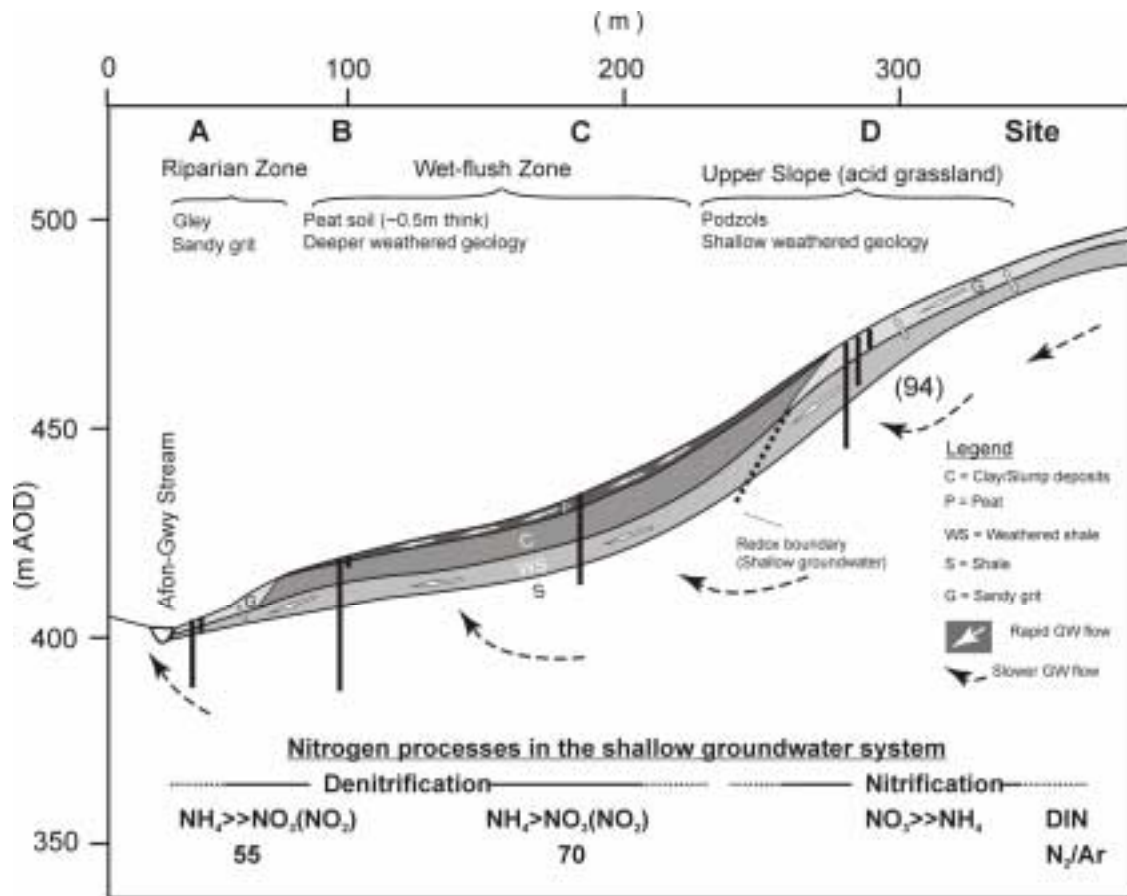Figure 10. Conceptual model of DIN processes and transformations

Table 1. Sample sites and location

Site	Easting	Northing	Setting	Depth (m)
Rainfall				
Composite sample from rainfall collectors in the Gwy and Hafren				
Soilwaters				
SW-A1,2	281980	285920	Riparian zone	0.1, 0.4
SW-B1,2	281895	285875	Wetland interfluve	0.1, 0.4
SW-C1,2	281824	285824	Wetland interfluve	0.1, 0.4
SW-D1,2,3	281792	285800	Upper hill slope	0.1, 0.2, 0.4
Groundwaters				
GW-A1,2*	281880	285700	Riparian zone	1.5, 9.0
GW-B1,2*	281900	285730	Wetland interfluve	0.5, 27.5
GW-C1,2*,3*	282030	285898	Wetland interfluve	2.0, 4.5, 12.5
GW-D1,2*	281990	285810	Upper hill slope	2.6, 15.7
GW-E1,2	282000	285460	Wetland interfluve	1.5, 10
GW-F1*,2	281990	285500	Wetland interfluve	1.0, 10
GW-G1,2	281820	285300	Upper hill slope	5.0, 20
GW-H1,2	280800	286080	Riparian zone	5.1, 10.3
GW-I1,2	280875	286020	Upper blanket peat	2.3, 15.5
Pipeflow				
PF-A	282500	286200	Upper hill slope	
PF-B	282450	286000	Upper hill slope	
Streams				
Afon Gwy	280790	286109	Mid catchment	
Nant Cerrig	281870	285690	Upper catchment	

SW=Soil water, GW = groundwater, PF=Pipe flow . * Artesian Flow

Table 2. Summary results for nitrogen chemistry and dissolved organic carbon

Site	TON µg/L	NH$_4$-N µg/L	NO$_2$-N µg/L	DON µg/L	DOC mg/L	% DON*
Rainfall	173	199	-	87	0.6	19
SW-A	15	10	-	250	4.0	91
SW-B	10	10	-	260	5.2	93
SW-C	10	<5	-	250	4.2	95
SW-D	20	10	-	300	5.9	91
GW-A1	86	214	5.2	294	1.1	50
GW-A2	<5	38	<1	208	0.4	84
GW-B1	33	139	2.5	382	2.9	69
GW-B2	<5	6	<1	361	0.5	98
GW-C1	<5	8	<1	494	2.8	98
GW-C2	17	28	1.7	320	2.1	88
GW-C3	<5	9	<1	217	0.7	95
GW-D1	207	8	<1	269	2.2	56
GW-D2	3	11	<1	330	0.7	96
GW-E1	78	420	8.1	434	1.3	47
GW-E2	<5	72	<1	366	3.2	83
GW-F1	<5	218	2.6	567	2.1	72
GW-F2	16	28	<1	301	1.2	87
GW-G1	747	<2	<1	998	2.2	57
GW-G2	16	31	2.4	779	2.8	94
GW-H1	107	<2	<1	326	4.3	75
GW-H2	8	20	<1	405	10.6	94
GW-I2	137	<2	<1	647	1.3	82
PF-A	551	21	<1	1390	8.4	71
PF-B	58	12	1.2	240	4.1	77
Afon Gwy	53	5	<1	408	2.6	88
Nant Cerrig	105	29	<1	196	2.0	59

Data: median results from period June 2002 - May 2003, one off samples for pipe flow
*Conservative estimate: if median DON data <DL, value of half DL has been substituted, expressed as a % of the total dissolved nitrogen.

Table 3. Dissolved gases in groundwater

Site	Jan 2004 N_2O $\mu g/L$	March 2004 N_2O $\mu g/L$	N_2/Ar
GW-A2	<1	5.1	55.1
GW-B1	<1	11.5	41.1
GW-B2	<1	-	-
GW-C1	-	15.7	69.9
GW-C3	-	17.7	53.9
GW-D1	<1	-	-
GW-D2	<1	-	-
GW-G1	56.7	-	-
GW-I2	8.7	-	-

Cover Letter

14th February 2007

<div align="right">

British Geological Survey
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Dear Sir or Madam,

Please find attached a manuscript, tables and figures for a full-length article entitled 'Groundwater nitrogen transformations within a moorland catchment, mid-Wales'.

Yours Faithfully

Dan Lapworth