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Upland streamwater nitrate dynamics across decadal to sub-daily timescales: a case study of Plynlimon, Wales

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Abstract

Streamwater nitrate dynamics in the River Hafren, Plynlimon, mid-Wales were investigated over decadal to sub-daily timescales using a range of statistical techniques. Long-term data were derived from weekly grab samples (1984–2010) and high-frequency data from 7 hourly samples (2007–2009) both measured at two sites: a headwater stream draining moorland and a downstream site below plantation forest. This study is one of the first to analyse upland streamwater nitrate dynamics across such a wide range of timescales and report on the principal mechanisms identified. The data analysis provided no clear evidence that the long term decline in streamwater nitrate concentrations was related to a decline in atmospheric deposition only; nitrogen deposition first increased and then decreased during the study period. Increased streamwater temperature and denitrification may also have contributed to the decline in stream nitrate concentrations, the former through increased N uptake rates and the latter resultant from increased dissolved organic carbon concentrations. Strong seasonal cycles, with concentration minimums in the summer, were driven by seasonal flow minimums and seasonal biological activity enhancing nitrate uptake. Complex diurnal dynamics were observed, with seasonal changes in phase and amplitude of the cycling, and the diurnal dynamics were variable along the river. At the moorland site, a regular daily cycle, with minimum concentrations in the early afternoon, corresponding with peak air temperatures, indicated the importance of instream biological processing. At the downstream site, the diurnal dynamics were a composite signal, resultant from advection and nitrate processing in the soils of the lower catchment. The diurnal streamwater nitrate dynamics were also affected by drought conditions. Enhanced diurnal cycling in spring 2007 was attributed to increased nitrate availability in the post-drought period as well as low flow rates and high temperatures over this period. The combination of high-frequency short-term measurements and long-term monitoring provides a powerful tool for increasing understanding of the controls of element fluxes and concentrations in surface waters.

1 Introduction

Nitrogen (N) is a key nutrient in river-systems worldwide and an over-enrichment of N can lead to the problems of eutrophication, acidification and reduced biodiversity (e.g. Dise et al., 2009; Galloway et al., 2004; Jarvie et al., 1998; Neal and Jarvie, 2005; Smith et al., 1999; Stevens et al., 2006; Sutton et al., 2011; UK-NEA, 2011; Wright et al., 2001). Within aquatic environments nitrate (NO_3) is generally the dominant N fraction, with dissolved organic N (DON) an important component, particularly on a seasonal basis (Chapman et al., 2001; Reynolds and Edwards, 1995; Sutton et al., 2011). NO_3 has been studied extensively across the world, using process studies at single sites, long term monitoring of individual catchments such as Hubbard Brook in the USA (Likens, 2004), and integrated networks of monitoring sites such as the US Long-Term Ecological Research Network (http://www.lternet.edu/) and the UK Environmental Change Network (http://www.ecn.ac.uk). These studies have yielded important information on the N cycle but key areas of uncertainty remain. In particular, there is continued debate about the long-term effect of N deposition on catchment N processing within the context of other environmental variables such as air temperature and soil and streamwater carbon (C). The relative importance of soil and instream processing in the determination of instream N concentrations also remains poorly understood.

Streamwater NO_3 concentrations in forested catchments in New Hampshire, USA have declined remarkably over the last 30 yr (e.g. Goodale et al., 2003; Bernal et al., 2012). Commensurate with this decline was a very modest (and not statistically significant) decline in atmospheric N deposition (Bernal et al., 2012), and given this slight reduction only, the reduction in forest growth and an apparent accumulation of N in the terrestrial catchment were expected to increase stream N concentrations. Possible reasons for this unexpected decrease in streamwater NO_3 concentrations are debated and hard to distinguish given current monitoring regimes. The reasons offered include climate variability affecting soil temperature regimes, both gradually and in relation to the frequency of extreme events such as frosts; forest disturbances such as insect defoliation and ice storms; changes in forest species composition; long-term responses to forest harvesting; and subtle changes in stream N processing due, for instance, to more organic debris dams in the rivers, leading to increases in denitrification and particulate N export (see e.g. Goodale et al., 2003; Bernhardt et al., 2005; Bernal et al., 2012). Clearly, work is needed to better understand the relationship between deposition and streamwater concentrations.

Assumptions that N cycle processes in the terrestrial catchment are the overwhelming influence on stream NO_3 concentrations and export rates, and that instream processing is insignificant, no longer seem tenable (Bernhardt et al., 2005). A meta-analysis of studies in which both soil solution and adjacent stream NO_3 concentrations were measured demonstrated that, in undisturbed forested catchments, stream NO_3 concentrations typically were about half those in the below rooting-zone soil-solutions (Sudduth et al., 2013). This result indicates the importance of instream or near-stream N removal mechanisms. A recent review of river bed N removal mechanisms demonstrated the potentially large flux transfers between the water column and hyporheic zone, and a close connection of the C and N cycles (Trimmer et al., 2012). Thus, work is needed to better understand whether soil, groundwater and instream processes are the key control on the observed water chemistry.

To characterise instream NO_3 dynamics and the linkages between anthropogenic and climatic variability and the associated instream response, it is necessary to sample at frequencies capable of capturing the abiotic and biotic controls on water quality (Hood et al., 2006; Kirchner et al., 2004; Pellerin et al., 2009). Traditionally, water quality monitoring programmes involve discrete grab sampling at weekly to monthly intervals; however water quality determinands are known to vary considerably over much shorter time scales (e.g. Herrman et al., 2008; Nimick et al., 2011; Palmer-Felgate et al., 2008; Pellerin et al., 2012). Those studies that measure sub-daily instream NO_3 dynamics tend to be based on short term monitoring schemes, spanning a few days or specific months (e.g. Duff et al., 2008; Mulholland et al., 2006; Parker et al., 2007; Pellerin et al., 2009; Scholefield et al., 2005). These studies have also tended to focus on single site installations and often measurements have only been made during one hydrological year (e.g. Chapin et al., 2004; Ferrant et al., 2012; Parker et al., 2007). Whilst these studies are pioneering in many ways, the short durations of data makes the evaluation of the observed sub-daily dynamics and their importance to the overall NO_3 cycle difficult to quantify as it is not possible to place the dynamics within the wider context of NO_3 variability.

The aim of this paper is to help advance the understanding of the controls on NO_3 concentrations in streams, specifically their variation along the river system across a range of time scales from decades to hours. This was achieved through a detailed investigation of both long-term NO_3 measurements and periods of high-frequency NO_3 measurements for two sites on the River Hafren at Plynlimon in Wales. The long-term data were derived from weekly grab samples (1984–2010) and high-frequency data from 7 hourly samples during 2007–2009 (Neal et al., 2012, 2013). The Hafren dataset offers a unique ability to assess aspects of NO_3 cycling which previous datasets have not allowed. The long-term hydrochemical records allow the high-frequency dynamics observed within the 7 hourly dataset to be placed within the context of long-term hydrological changes, and how the instream dynamics are changing year to year. In addition, the collection of data from two sites on the same river also allows an evaluation of how the high-frequency nutrient dynamics change along the system. The paper discusses what can be concluded about the principal mechanisms controlling the observed streamwater NO_3 dynamics along the River Hafren using both low- and high-frequency data, with particular focus on the controls on long term changes in the streamwater nitrate concentrations and the relative importance of soil and instream processes in the control of the observed water chemistry.

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2 Study area and data resources

2.1 Study area

All the data presented in this paper were collected by the Centre for Ecology and Hydrology (CEH) in the upper River Severn, Plynlimon, mid-Wales (Fig. 1 and Table 1). The hydrology and hydrochemistry of this catchment have been studied extensively over the last 40 yr (Green and Marsh, 1997; Marc and Robinson 2007; Neal, 1997, 2004). This study focuses on a small stream, the Hafren, which drains one of the main subcatchments of the Plynlimon catchment and forms the headwaters of the River Severn (Neal et al., 2001; Shand et al., 2007, 2005).

The Hafren catchment has an area of 3.6 km^2 (of which the Upper Hafren is 1.2 km^2) with an altitudinal range of 355–670 m (Brandt et al., 2004; Marsh and Hannaford, 2008). The bedrock geology is base-poor and comprises fractured Lower Palaeozoic slates, mudstones, greywackes and sandstones (Foster et al., 2001; Godsey et al., 2010). The landscape has been influenced by Quaternary glaciation, with periglacial activity leaving remnants of locally-derived overlying boulder clay and till (Brandt et al., 2004; Neal et al., 2010). The predominant soils are stagnopodzols, but acidic peat, acid brown earths and stagnogleys also occur, and are typically less than 1 m thick (Foster et al., 2001; Neal et al., 2005). Peat erosion has also resulted in significant hag formation in the upper reaches of the catchment (Neal et al., 2010).

The catchment is divided into two subcatchments: the Upper and Lower Hafren (Fig. 1). The Upper Hafren is predominately semi-natural moorland with areas of low intensity sheep grazing (Fig. 1, P1; Neal et al., 2010). No fertilisers are applied and the land is not actively managed. The vegetation cover is predominantly a dwarf shrub heath community, dominated by *Calluna vulgaris* and *Eriophorum* spp., with acid grass species, *Nardus stricta* and *Festuca* spp., on steeper slopes and gullies (Fig. 1). The whole sub-catchment has been designated as a Site of Special Scientific Interest. The lower half of the catchment is first generation plantation forestry, consisting of mainly *Picea sitchensis* (Sitka spruce) (Fig. 1, P2–4). The catchment was planted in several phases between 1942 and 1964 and, although no nitrogen fertilisation has taken place, the forest received aerial applications of potash (200 $kg\,ha^{-1}$) and phosphate (375 $kg\,ha^{-1}$) between September and November 1974 (Neal et al., 2010; Newson, 1976; Reynolds et al., 1989). Over the last 25 yr the Lower Hafren catchment has been thinned and clear-felled in several phases, with cleared areas replanted with juvenile Sitka spruce (Neal et al., 2005, 2011; Whitehead et al., 2004). There is no human habitation in the catchments and no registered consented discharges.

The Hafren river channel is shallow, rocky, steep and irregular (Fig. 1; Newson and Harrison, 1978). The streambed substrate consists largely of boulders, cobbles, pebbles and exposed bedrock (Fig. 1; Kirby et al., 1991; Newson and Harrison, 1978). The aquatic vegetation of the system has been studied, throughout the last twenty years, as part of the UK Acid Waters Monitoring Network (Kernan et al., 2010). Throughout this time, the epilithic diatom community has been dominated by one acidobiontic species, optimal pH < 5.5, *Eunotia exigua*, with *Tabellaria flocculosa* becoming increasing prevalent since 2005 and *Fragilaria virescens* present since 2008 (Kelly et al., 2005; Kernan et al., 2010; Shilland et al., 2012). Under the EU Water Framework Directive (WFD) the river is classified as "high" status (the top category) for its diatom communities (Ecological Quality Ratio (EQR) ≥ 0.93). This means that, based on measurements of River Trophic Diatom Index, the River Hafren diatom community is close to the natural state anticipated in an undisturbed system (WFD 2008). Recent work by Ledger and Hildrew (2005) identified cyanobacteria in the river. Filamentous green algae have been present on the river regularly since 2005 and the aquatic moss *Hyocomium armoricum* has also been identified (Kernan et al., 2010; Shilland et al., 2012). The aquatic macrophyte community is largely limited to *Scapania undulata*, an acid tolerant leafy liverwort species (Kernan et al., 2010).

2.2 Environmental conditions

Situated on the upper slopes of Pumlumon Fawr, 24 km inland from the Irish Sea, the catchment has a temperate maritime climate dominated by westerly frontal sys-

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tems. Atmospheric deposition is largely derived from sea salts and is relatively unpolluted (Reynolds et al., 1999). Mean wet N deposition was 6.1 (NO_3) and 9.1 (NH_4) kg N ha^{-1} yr^{-1} (2007–2009) derived from long-range transport (Department for Environment, Food and Rural Affairs (DEFRA), 2012). Pembroke Power Station, (located 80 km to the southwest) may have also contributed to atmospheric deposition before it ceased generating electricity in 1997 (RWE npower, 2012). Between 1980 and 2010, mean annual precipitation and air temperature were 2600 mm yr^{-1} and 7 °C respectively at the Carreg Wen Automatic Weather Station (AWS) (Fig. 1). Annual evapotranspiration losses were estimated to be between 500–700 mm yr^{-1} (Hudson et al., 1997a). Flows respond rapidly to rainfall events, varying over two orders of magnitude from 0.01 to 7.3 m^3 s^{-1} (based on the Lower Hafren gauging station flow record between 1980 and 2010). Between 1980 and 2010, median flow at the Lower Hafren gauging station was 0.13 m^3 s^{-1}. Flow and air temperature exhibited seasonal patterns with flows lowest in the summer months when air temperature is highest (Fig. 2).

Prior to the commencement of the high-frequency monitoring scheme, in March 2007, the Plynlimon catchment experienced a prolonged period of below average rainfall. At Plynlimon, between June 2003 and September 2006, the monthly rainfall volumes recorded at the Carreg Wen AWS were on average 12 % lower than the long-term monthly rainfall volumes (1980–2010), with differences of 67 % in August 2003 and 65 % in June 2006. As a result, recorded flows at the Lower Hafren gauging station were significantly lower than long-term average flows over this period (Fig. 2). Air temperatures were also elevated during this period and remained high into early 2007 (Fig. 2). This drought was then followed in 2007 by one of the UK's wettest summers on record. In July 2007, the median flow at the Lower Hafren gauging station was 0.33 m^3 s^{-1}, almost 5 times higher than the long-term median flow experienced in July of 0.07 m^3 s^{-1} (Environment Agency, 2007; Marsh, 2007; Marsh et al., 2007).

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2.3 Data resources

There are two discharge gauging stations within the Hafren catchment which are located at the outflows from the upper and lower subcatchments (Fig. 1 and Table 1). Flows at the Lower Hafren flume have been recorded since 1976, with weekly chemical sampling beginning in 1983. Chemical sampling commenced at the Upper Hafren in 1990, at the upper boundary of the Hafren forest, but flows have only been recorded at this site since 2005 (Neal et al., 2010). Flows for the Upper Hafren site, for the period between 1990 and 2005, were estimated using the flows recorded at the Lower Hafren gauging station, as a strong linear correlation was identified between the flows at both stations ($U_{Haf} = 0.0152(\pm 0.0001) + L_{Haf} \times 0.3468(\pm 0.0002)$; $r^2 = 0.97$, $p < 0.001$, $N = 200\,152$) (Neal et al., 2010). Water quality samples were collected directly upstream of the flow gauging station in the Lower Hafren (Fig. 1). In the Upper Hafren, due to the logistics of accessing the river from the flume location, water quality samples were collected approximately 150 m upstream of the flume, above the Hafren forest edge. The two monitoring points are located approximately 2.5 km apart (Fig. 1).

In addition to the flow and streamwater chemistry data, hourly near-surface (2 m) air temperature, incoming solar radiation and rainfall volumes were recorded at the Carreg Wen AWS since 1976. Weekly rainfall and cloud water chemistry data are also available from 1983 and 1990 respectively, and 7 hourly rainfall chemistry data are available between 2007 and 2009 (Table 1). Streamwater temperature measurements were made as part of the long-term monitoring scheme, but not the high-frequency monitoring scheme. Hourly air temperature recorded at the Carreg Wen AWS was therefore used as a surrogate for streamwater temperature, at both sites, to facilitate an assessment of the relationship between NO_3 and temperature in the high-frequency time-series.

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3 Methods

3.1 Data collection

The long-term catchment monitoring was undertaken by collecting weekly grab samples, usually on the same day of each week, and then returning them to the laboratory for analysis. The same sampling route was followed on each site visit with the Lower Hafren sample collected first and the Upper Hafren sample approximately 1 h later (Brandt et al., 2004). The high-frequency monitoring scheme employed Xian automatic samplers within the field, at the same locations as the long-term monitoring points. The samplers were run on a 24 bottle programme, collecting 500 mL samples at 7 h intervals. The sample bottles were changed weekly and, as with the long-term monitoring, returned to the laboratory for processing (Neal et al., 2012).

All water quality samples were analysed for a wide range of chemical determinands including the major ions, nutrients, trace elements, pH, alkalinity and conductivity. For the purpose of NO_3 analysis, under the long-term monitoring programme the weekly samples were filtered in the field using a 47 mm GF/C glass fibre filter into pre-cleaned glass bottles (chromic acid leached and distilled/deionised water), that were rinsed with filtered sample prior to sample storage. For the high-frequency monitoring programme, samples were filtered in the laboratory using a PALL Lifesciences AcroCap filter with a 0.45 µm Supor® membrane pre-cleaned with distilled/deionised water and rinsed with filtered sample before storage. For both monitoring programmes, sample NO_3 concentrations were determined by ion chromatography using the ICS-2000 system. The accuracy of the determinations were evaluated using materials supplied by the Aquacheck LGC Interlaboratory Proficiency Testing Scheme (see the supplementary data accompanying Neal et al. (2013) for further details of the sampling procedure, analysis methodology and links to the freely accessible complete hydrochemical datasets).

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3.2 Data pre-processing

All the datasets used include periods of missing data. Within the long-term monitoring programme there were occasional times when sample collection was not done. These were the weeks preceding and following Christmas, a three month period caused by restricted site access during the 2001 Foot and Mouth disease outbreak and rare occasions when heavy snowfall prevented site access (Cooper, 2004; Neal et al., 2003). During the high-frequency monitoring programme, samples were collected at 7 h intervals whenever possible, however occasionally samples could not be taken due to monitoring equipment malfunction. The time-series analysis techniques used here are designed to cope with data which include missing values and therefore infilling of missing values was not done. In all cases the raw observed time-series have been analysed, no smoothing, averaging or infilling has taken place.

3.3 Time-series decomposition

All NO_3 time series were investigated using standard exploratory data analysis techniques such as time-series plots, calculation of summary statistics, distribution analysis, and correlation and linear regression analysis. Time series of the difference in concentration between the lower and upper monitoring points were also used to investigate the NO_3 dynamics along the river continuum, Eq. (1):

$$C_{\mathrm{d}_i} = C_{\mathrm{L}_i} - C_{\mathrm{U}_i} \tag{1}$$

where C_d is the difference in concentration between the Upper Hafren (C_U) and Lower Hafren, (C_L) at time i. The concentration difference time series were analysed to determine if the median concentration difference was statistically different from zero, for the complete time series and for baseflow and stormflow time-series subsets where stormflows are defined as those flows greater than the 90th percentile flow and baseflows are those less than the 10th percentile.

The MATLAB®-compatible CAPTAIN Toolbox, developed at Lancaster University for non-stationary time-series analysis, was used to explore the datasets (MathWorks, 2009; Young et al., 2007). The NO_3 time series were analysed to assess long-term trends, seasonality and shorter-term cyclical signals. This analysis was undertaken using Dynamic Harmonic Regression (DHR) analysis (Ciavatta and Pastres, 2011; Keery et al., 2007; Taylor et al., 2007; Young, 1998; Young et al., 1999, 2007). DHR is a special case of the Unobserved Component model, which decomposes an observed time-series into its component parts (Halliday et al., 2012; Pedregal and Trapero, 2007; Taylor et al., 2007; Young et al., 1999, 2007):

$$y_t = T_t + S_t + C_t + e_t \qquad e_t \sim N(0, \sigma^2) \tag{2}$$

y_t is the observed time-series; T_t is the trend; S_t seasonal component; C_t is a sustained cyclical component with a period separate from the seasonal component; and e_t is an "irregular" component, defined in Eq. (2) as a random sequence from a Normal distribution with zero mean, and variance σ^2.

The trend, T_t, was defined using an Integrated Random Walk (IRW) model (Taylor et al., 2007; Young et al., 2007). An IRW is a special case of the Generalised Random Walk (GRW) in which the parameters $\alpha = \beta = \gamma = 1$ and $\delta = 0$, and has been demonstrated to be useful for extracting smoothed trends from non-stationary long-duration time series, Eq. (3) (Ciavatta and Pastres, 2011; Young et al., 2007):

$$\begin{aligned} T_t &= \begin{pmatrix} 1 & 0 \end{pmatrix} \begin{pmatrix} x_{1t} \\ x_{2t} \end{pmatrix} \\ \begin{pmatrix} x_{1t} \\ x_{2t} \end{pmatrix} &= \begin{pmatrix} \alpha & \beta \\ 0 & \gamma \end{pmatrix} \begin{pmatrix} x_{1t-1} \\ x_{2t-1} \end{pmatrix} + \begin{pmatrix} \delta \\ 1 \end{pmatrix} \eta_{t-1} \end{aligned} \tag{3}$$

T_t is the identified trend, consisting of the first state x_{1t}; x_{2t} the second state, is the slope of the trend; and η_{t-1} is a zero mean, serially uncorrelated white noise variable (Young et al., 2007). The trend was defined as statistically significant if the corresponding

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values of the slope parameter, x_{2t}, were different from 0, i.e. no change in the slope of the trend line, at a confidence level of 95 %, Eq. (3) (Becker et al., 2006; Ciavatta and Pastres, 2011).

The periodic components, S_t and C_t, were defined as (Taylor et al., 2007; Young et al., 2007):

$$\sum_{i=1}^{R} \{a_{i.t}\cos(w_i t) + b_{i.t}\sin(w_i t)\} \tag{4}$$

$a_{i.t}$ and $b_{i.t}$ are stochastic time-varying parameters, which define the phase and amplitude of the seasonal/cyclic component, and were modelled as GRW processes. As these parameters can vary with time, this allowed for non-stationarity within the seasonal and short-term dynamics (Chappell and Tych 2012). w_i, $i = 1,2,\ldots,R$, are the fundamental and harmonic frequencies associated with the periodicity in the observed time-series chosen by reference to the spectral properties of the series. For the long-term NO_3 time-series the only periodicities identified were associated with the period 52, which corresponded directly to an annual cycle under the weekly sampling regime. The trend component, T_t, and periodic components, S_t and C_t, can be modelled simultaneously by the inclusion of a frequency of zero in the DHR analysis. This reduced Eq. (4) to $a_{i.t}$, which is the modelled as an IRW processes, as outlined above.

Under the 7 h sampling regime, 24 samples were collected per week, and within each week every hour of the day was sampled once (Neal et al., 2012). Accurately interpreting the diurnal dynamics from this 7 hourly data is complex because the data do not contain sufficient information to fully characterise the dynamics at this frequency. For example, if the NO_3 signal exhibits a single peak diurnal cycle, as identified in other catchments (Nimick et al., 2011), under the 7 hourly regime the diurnal cycle peak and minimum will only be captured once a week and on different days (Halliday et al., 2012). DHR analysis was therefore used to model the expected diurnal cycle based on the information contained in the 7 hourly data. This was achieved using an hourly time-series as input to the DHR analysis. This hourly time-series was based on the 7

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hourly data with the 6 time steps between each recorded sample assigned the MATLAB missing value code (NaN). The 7 hourly data were not interpolated.

High-frequency monitoring was only undertaken for one year at the Lower Hafren monitoring point, between March 2007 and March 2008, and, due to sampling equipment failure, samples were not collected between late May and July 2007. The diurnal cycle analysis was therefore restricted to a subset of data, which allowed the direct comparison of dynamics at the upstream and downstream sites and limited the analysis to the spring and early summer when diurnal NO_3 dynamics were most evident (Fig. 5; Nimick et al., 2011):

- 6 March 2007 19:00 GMT–6 May 2007 11:00 GMT (62 days) – referred to here after as Spring 2007

The monitoring project was extended in the Upper Hafren until January 2009. Therefore, the diurnal cycle analysis was also undertaken on the same time period in 2008, to facilitate an examination of how the diurnal NO_3 dynamics varied between the two monitoring years:

- 6 March 2007 20:00 GMT–6 May 2007 05:00 GMT (62 days) – referred to here after as Spring 2008

Under DHR, parameter optimisation was undertaken in the frequency domain, and used the spectral properties of the model, to optimise the parameters such that the logarithm of the model spectrum fits the logarithm of the empirical pseudo-spectrum of the raw time-series in a least squares sense (Young et al., 1999, 2007; Keery et al., 2007). The model parameters were estimated recursively using the Kalman Filter and the Fixed Interval Smoother. The recursive nature of this procedure allows for the handling of missing values so the pre-processed data can be analysed directly (Chappell and Tych, 2012; Romanowicz et al., 2006).

4 Results

Within the Hafren catchment, NO_3 was the dominant form of streamwater N, accounting for approximately 52 % of the total dissolved nitrogen (TDN); with nitrite (NO_2) accounting for less than 1 %, ammonium (NH_4) for approximately 10 % and dissolved organic nitrogen (DON) approximately 37 % (based on the long-term annual average concentrations recorded under the weekly monitoring programme). Seasonal variability in the dominance of different N fractions was observed (Chapman et al., 2001). In the winter months, NO_3 accounted for approximately 76 % of the TDN between December and February at both sites. Between June and August, DON became more important, accounting for approximately 51 % of the TDN.

Detailed analysis of the N dynamics of the Hafren stream was restricted to NO_3. DON measurements were limited in both the long-term and high-frequency datasets and although high-frequency variability was visible in the observations, this appeared dominated by flow event responses with no identifiable, regular, cyclical pattern (Fig. 3). In this upland N-limited system most NH_4 is retained by plant uptake and chemical absorption (Peterson et al., 2001), and, as with DON there was no identifiable, regular, cyclical diurnal pattern within the high-frequency NH_4 time-series.

4.1 Long-term catchment NO_3 dynamics

4.1.1 NO_3 trends

Streamwater NO_3 concentrations in the Hafren were low, $< 1\,mg\,N\,L^{-1}$, (Figs. 4 and 5; Table 2) compared to concentrations of up to $14\,mg\,N\,L^{-1}$ reported within some agricultural European catchments (Sutton et al., 2011), but higher than some more pristine areas (the Upper Hafren is about the 38th percentile in the survey by Sudduth et al., 2013). Significant trends were identified within the long-term streamwater NO_3 time-series at both monitoring locations (Fig. 6). In the Upper Hafren there was a decreasing long-term trend, with mean annual concentration decreasing from $0.26\,mg\,N\,L^{-1}$ (1991)

to 0.14 mg N L^{-1} (2010; Fig. 6a). In the Lower Hafren, the overall NO_3 trend was a decline, with a change in mean annual concentration from 0.31 to 0.15 mg N L^{-1} (1984–2010), however the extracted underlying trend showed an increase between 1993 and 2001 (Fig. 6b).

There were no significant trends in the catchment flow rates, rainfall volumes or cloud water deposition volumes over the study period. However, analysis of the inorganic N deposition ($NO_3 + NH_4$) at the Carreg Wen AWS revealed a marked shift in N deposition dynamics over the period of record. Non-significant increasing trends were observed in inorganic N concentrations in the rainfall and cloud water between 1983/1990 and 1997, with mean annual rainfall concentrations increasing from 0.62 to 0.89 mg N L^{-1} and cloud water concentrations from 9.18 to 10.81 mg N L^{-1}. This was then followed by non-significant declining trend between 1998 and 2010, with mean annual concentrations falling to 0.37 and 6.22 mg N L^{-1} in the rainfall and cloud water respectively, by 2010. The marked reductions in rainfall and cloud water N concentrations after 1997 (Fig. 4a, b), are possibly caused by decreased atmospheric deposition associated with the closure of Pembroke Power Station (RWE npower, 2012), but may also be related to changes in weather patterns.

Streamwater temperature increased over the study period, from an annual mean of 7.2 and 6.9 °C at the Upper and Lower Hafren respectively in 1991, to annual means of 8.9 and 8.7 °C in 2010. Part of this increase may have been driven by a move towards later sampling times over the course of the study period. At both sites the average annual sample time changed by 1 h, from 09:00 to 10:00 GMT at the Lower Hafren and from 10:00 to 11:00 GMT at the Upper Hafren between 1990 and 2010, with a marked step change in 1999. Over this time the mean streamwater temperature difference was 0.5 °C between 09:00 and 10:00 GMT and 0.4 °C between 10:00 and 11:00 GMT. As the observed increase in streamwater temperature is greater than the change had it been driven purely by changing sampling time, this suggests that the increasing trend in streamwater temperature is real.

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4.1.2 Upstream–downstream dynamics

The long-term concentration difference time-series showed that overall NO_3 concentrations were higher at the Lower Hafren monitoring point, with a median concentration of 0.24 $mg\,N\,L^{-1}$ compared to 0.17 $mg\,N\,L^{-1}$ (Fig. 4g). The difference between median concentrations at both sites was statistically significant (Mann-Whitney *U* test, $p < 0.001$; Table 2; Fig. 7). The distributions of the NO_3 concentrations at both sites were also statistically different, with the range in NO_3 concentrations greater at the Lower Hafren site, 1.33 $mg\,N\,L^{-1}$, than at the Upper Hafren, 1.02 $mg\,N\,L^{-1}$ (Two-sample Kolmogorov-Smirnov test: $p < 0.001$; Fig. 7).

There was a strong positive correlation between the NO_3 concentrations in the Upper and Lower Hafren in long-term time series (Fig. 7c):

$$L_{Haf_W} = 0.949 \times (U_{Haf_W}) + 0.065 \qquad r^2 = 0.56; \quad p < 0.001; \quad N = 1006 \tag{5}$$

NO_3 concentrations in the Hafren showed significant correlations with a number of other determinands recorded as part of the long-term monitoring scheme (Table 3). In general the relationships were largely consistent between the upstream and downstream monitoring points, with positive correlations with atmospherically derived determinands such as chloride (Cl) and sodium (Na) and negative correlations with streamwater temperature and alkalinity (Table 3).

At Plynlimon, stormflow streamwater is acidic with elevated aluminium (Al) and dissolved organic carbon (DOC) concentrations and decreased calcium (Ca) and silicon (Si) concentrations, indicating the dominance of acidic upper soil water; these relationships are reversed under baseflow conditions (Soulsby and Reynolds, 1993; Halliday et al., 2012; Neal et al., 2011, 2012). Under stormflow conditions, the difference in NO_3 concentration between the lower and upper monitoring sites doubled from 0.03 to 0.07 $mg\,N\,L^{-1}$ (Table 4). This observation suggests that under stormflow conditions water from the upper soil horizons, delivered from the forested lower reaches of the catchment, has elevated NO_3 concentrations, and provides a source of NO_3 to the streamwater which is not present in the soil water derived from the purely moorland upper reaches. This conclusion is supported by the positive correlation between Al and NO_3 in the Lower Hafren which is not present at the Upper Hafren site (Table 3), Al being a marker for soil water at Plynlimon.

4.2 Seasonal NO_3 dynamics

Strong seasonal signals dominated the streamwater NO_3 time-series at both the Upper and Lower Hafren, with a strong positive correlation between the mean monthly NO_3 concentrations at both sites ($\rho = 0.79$; $p < 0.001$; Fig. 6 and Table 5). At both monitoring points, although there was slight variability in the exact phase of the seasonality, the overall pattern was consistent with peak NO_3 concentrations occurring in the winter months, between January and February, and the minimum concentrations occurring in the summer months, between July and August. The amplitude of the seasonality, at both sites, closely followed the overall trend in the streamwater NO_3 concentrations. In the Upper Hafren, the amplitude of the seasonal cycle decreased through the period of record, but the cycle was nonetheless very strong, accounting for on average 62 % of the annual range in NO_3 concentrations (Table 5). Overall, the amplitude of the Lower Hafren seasonal NO_3 cycle also decreased over the study period, however periods of greater seasonal variability were observed between 1996 and 1998 and between 2001 and 2004 (Fig. 6).

A seasonal cycle could not be extracted from the rainfall volume or the cloud water deposition volumes. In addition, there was no extractable seasonal cycle in the catchment N inputs, in terms of rainfall or cloud water NO_3 and NH_4 concentrations. Strong seasonal cycles were observed within the flow, streamwater temperature and incoming solar radiation time series. The flow seasonality exhibited a strong and consistent phase at both sites and was in phase with the NO_3 seasonality, with peak flows in the winter and minimum flows in the summer. There was variability in the amplitude for the flow seasonality at both sites, with increasing amplitude associated with periods of extreme rainfall, such as the winter of 1998 (Fig. 4c, e). Streamwater temperature and solar radiation exhibited seasonality with the opposite phase to NO_3, with peak streamwater temperatures and incoming solar radiation in the summer months, between June and August, and minimums in the winter months, between December and February. The identified seasonality was very strong for both determinands, contributing on average 60 % to the annual variability (Table 5), and the cycle amplitudes were consistent throughout the study period.

4.3 Short-term variability in NO_3 dynamics

The high-frequency data revealed seasonal, event and diurnal variability in NO_3 concentrations. Within the context of the long-term NO_3 variability, both the Upper and Lower Hafren NO_3 concentrations were in decline between 2007 and 2009 (Fig. 6). The seasonal pattern identified in the high-frequency data was consistent with that identified in the long-term monitoring datasets, with concentration peaks in the winter months and minimums in the summer months (Fig. 5).

The high-frequency concentration difference time-series showed a slightly different pattern to the long-term data with NO_3 concentrations higher at the Upper Hafren monitoring point than at the Lower (Fig. 5e), with a difference in median concentration of $-0.02\,\mathrm{mg\,N\,L^{-1}}$, which more than triples under baseflow conditions to $-0.06\,\mathrm{mg\,N\,L^{-1}}$ (although small these differences were statistically different from zero; Table 4). The occurrence of higher NO_3 concentrations at the upper monitoring point during 2007 can also be seen in the long-term monitoring data when annual changes in the concentration differences are analysed (Figs. 4g, 5e and Table 4). The difference between NO_3 concentrations in the Lower and Upper Hafren under stormflow conditions is the same in the high-frequency data as the long-term data, with elevated concentrations evident at the lower monitoring point. These results indicate that, despite the small differences under baseflow conditions, under stormflow conditions the flows derived from the forested catchment still had a higher NO_3 concentrations than those coming from the moorland dominated catchment.

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Excluding spring 2007, at the Upper Hafren significant dilutions in NO_3 concentration were observed during high flow events, with concentrations dropping by over $0.15\,mg\,N\,L^{-1}$ from baseflow concentrations (Fig. 5c). In the Lower Hafren, despite the flow rates being almost 3 times higher than in the Upper Hafren, the level of dilution in response to high flow events was greatly diminished (Fig. 5d). These event dynamics support the observations made in the long-term datasets that the soil water derived from moorland upper reaches of the Hafren catchment was depleted in NO_3 in comparison to the soil water delivered from the forested lower reaches.

A strong degree of diurnal variability was visible in high-frequency NO_3 time-series at both the Upper and Lower Hafren (Fig. 5). The diurnal dynamics exhibited a seasonal pattern with dynamics strongest in the spring and summer months, when NO_3 concentrations were at their lowest (Figs. 8 and 9). The modelled diurnal dynamics provide a first means of investigating the complexity present in the high-frequency NO_3 data.

4.3.1 Diurnal dynamics: Spring 2007

During Spring 2007, streamwater NO_3 concentrations were higher at the Upper Hafren monitoring point than the lower, with a median difference of $-0.03\,mg\,N\,L^{-1}$ (Fig. 8 and Table 2). Streamwater NO_3 concentrations in the Upper Hafren were significantly correlated with a range of determinands (Table 3), exhibiting negative correlations with variables such as air temperature, solar radiation, pH and Ca and positive correlations with flow, DOC and Al. The Lower Hafren exhibited very similar correlations but with a weaker correlation with air temperature and no significant relationship with solar radiation (Table 3). These relationships differ from the relationships identified in the long-term record, where DOC was identified to be negatively correlated with NO_3 at both sites and both Ca and flow exhibited much weaker correlations with NO_3 (Table 3).

A single-peak diurnal NO_3 cycle was observed at both monitoring points. In the Upper Hafren, the modelled diurnal cycle phase was consistent, with peak NO_3 concentrations between 02:00 and 03:00 GMT and minimum concentrations between 14:00 and 15:00 GMT (Fig. 8 and Table 6). The amplitude of the cycle was very small at

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the beginning of the period, $< 0.01\,mg\,N\,L^{-1}$, and apart from a smaller amplitude during increased flow at the end of April, increased throughout the period to $0.07\,mg\,N\,L^{-1}$ (median standard error = 0.004). In the Lower Hafren, the diurnal cycle phase was less consistent, with the timing of peak and minimum concentrations varying throughout the period. At the start of the period, peak concentrations occurred at 04:00 GMT, 1 h later than peak concentrations occurred at the Upper Hafren, but by the end of the period they were occurring at 09:00 GMT, 7 h later than the Upper Hafren (Fig. 8; Table 6). The amplitude of the cycle again strengthened throughout, but the maximal amplitude reached was only $0.05\,mg\,N\,L^{-1}$ (median standard error = 0.005). The high NO_3 peaks observed between 23 and 24 April in the Lower Hafren time-series, associated with the delivery of NO_3 from the catchment during the high-flow event (Fig. 8b), do not significantly affect the modelled diurnal cycling, with the diurnal variability retained under these peaks.

Diurnal cycling was not identified in rainfall volume, N deposition, or flow rates at either site. However, as expected strong diurnal cycles were of course identified in the hourly air temperature and solar radiation time-series (Table 6). For air temperature, peak temperatures occurred at approximately 14:00 GMT and minimum temperatures at approximately 02:00 GMT, the opposite phase to the Upper Hafren diurnal NO_3 cycle. A positive relationship was evident between amplitude of the temperature and NO_3 diurnal cycles, indicating that as the diurnal variation in temperature increased so too did the variation in NO_3 concentration. For solar radiation, diurnal peaks occurred at 12:00 GMT followed by diurnal minimums during the night, when solar radiation is zero. This was also the opposite phase to the Upper Hafren NO_3 cycle, but minimum NO_3 concentrations lagged peak solar radiation by, on average, two hours.

4.3.2 Diurnal dynamics: Spring 2008

The modelled diurnal NO_3 cycle for the Upper Hafren in Spring 2008 period was weaker and more variable than the cycling identified in Spring 2007 (Fig. 9; Table 6). In Spring

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2008, the maximum amplitude of the diurnal NO_3 cycle in the Upper Hafren was only 0.03 mg N L^{-1} compared to 0.07 mg N L^{-1} in Spring 2007. In addition, the timing of peak concentrations varied between 23:00 and 03:00 GMT in Spring 2008, compared to between 02:00 and 03:00 GMT in Spring 2007. In Spring 2008, NO_3 also exhibited different relationships with other determinands than observed in Spring 2007. Principally, where in 2007 a strong positive correlation was found between flow and NO_3 ($\rho = 0.71$, $p < 0.0001$), no relationship was found in spring 2008 (Table 3). Furthermore, no significant correlations were found between NO_3 and Ca, Mg, Al or DOC, which in Spring 2007 had strong significant correlations with NO_3 (Table 3).

As in Spring 2007, no diurnal dynamics were identified in rainfall/cloud water volumes, N deposition, or flow time-series. Air temperature was more variable in Spring 2008, with the timing of peak diurnal temperatures varying between 08:00 and 17:00 GMT. In addition the amplitude of the diurnal variation was smaller, on average only 3.5 °C compared to 6.0 °C in 2007. The solar radiation diurnal cycle was very similar to that observed in Spring 2007.

5 Discussion

5.1 Drivers of long-term NO_3 dynamics

5.1.1 NO_3 trends

The main long-term trend was the decline in streamwater NO_3 concentrations over the study period at both sites (Sect. 4.1), with a decline of 46 % in the Upper Hafren (1991–2010) and 51 % in the Lower Hafren (1984–2010). The most likely explanation for the long-term NO_3 decline was lower atmospheric N inputs, supplemented by increased N uptake driven by increasing temperatures, and perhaps also linked to stimulation of hyporheic denitrification by increased DOC availability.

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Historic work within the Plynlimon catchment has related declining trends in streamwater NO_3 to declining atmospheric N deposition, associated with emission control legislation (Neal et al., 2001). Atmospheric N deposition is the only significant N input to the N-limited Hafren system, with the majority of deposition occurring as wet deposition (wet NO_3 and NH_4 deposition accounted for 67 % of the total N deposition at Plynlimon between 2007 and 2009: DEFRA, 2012). Although annual N deposition amounts are quite variable, the analysis demonstrated an increasing trend in rainfall and cloud water NO_3 and NH_4 concentrations up to 1997, followed by a declining trend. Overall the timing of the decline in stream NO_3 does not correlate exactly with the timing of the decline in atmospheric N deposition, with no increasing trend observed between 1990 and 1997. This situation is similar to that observed in the NE USA (e.g. Bernal et al., 2012). Therefore, although reductions in atmospheric deposition will have impacted on the streamwater NO_3 dynamics, additional factors may have also contributed to the declining trend.

Climate changes, such as increasing temperature, have also been linked to streamwater NO_3 trends in other systems (e.g. Bernal et al., 2012). At Plynlimon, increasing streamwater temperatures will have promoted increased NO_3 uptake by the diatom biofilms, bryophyte communities and cyanobacteria in the streambed and hyporheic zone (Ledger and Hildrew, 2005; Frame, 2010; Kernan et al., 2010; Shilland et al., 2012). The significant strong negative correlation identified between streamwater NO_3 and temperature (Table 3) and the temperature dependence of the seasonal and diurnal NO_3 variation (see below) support this. Assuming an exponential relationship between temperature and the rates of biological processes and that a 10 °C increase in temperature doubles the rate (following the Q_{10} model; Chapra, 1997, p. 40), the observed streamwater temperature change would increase uptake rates by approximately 12–16 % over the study period. Therefore, although this alone is insufficient to explain the decline in streamwater NO_3 concentrations, it likely will have played a contributory role in the long-term decline.

Nitrate may also be removed from the system by other temperature-sensitive processes, such as denitrification. Although, increased temperatures will have reduced oxygen supply slightly, denitrification in the Hafren flowing water is unlikely as the river is still a highly oxygenated system (Environment Agency, 2009). However, denitrification in microsites in the hyporheic zone may have occurred, stimulated by increased DOC availability (e.g. Trimmer et al., 2012). Streamwater DOC concentrations have increased in the Hafren on the same timescale as NO_3 has decreased (Halliday et al., 2012), and NO_3 and DOC are significantly negatively correlated (Table 3). The factors controlling denitrification in flowing waters are not well understood (see e.g. Trimmer et al., 2012), and further work is required to quantify the role this mechanism has played in the long-term streamwater NO_3 decline. Other hypotheses suggested elsewhere to account for declining NO_3 concentrations such as an increase in N storage, associated with woody debris dams, and recovery from catchment disturbances (e.g. Bernhardt et al., 2005; Bernal et al., 2012) are not applicable in the Upper Hafren catchment where there are no trees and land use change has not occurred. In addition, although cyclic meteorological phenomena such as the North Atlantic Oscillation (NAO) may have a subtle effect through altering hydrological pathways (Monteith et al., 2000; Ness et al., 2004), the NO_3 decline has continued through periods of both positive and negative NAO Index values.

5.1.2 Upstream–downstream dynamics and forest effects

In general, streamwater NO_3 concentrations were higher at the Lower Hafren monitoring site than the Upper (Fig. 4). This indicates that the forested lower reaches of the catchment were producing more NO_3. Forest planting on wet moorlands in the UK, as at Plynlimon, is achieved by extensive ditch cutting, with the trees being planted on upturned soil between the ditches (e.g. Reynolds and Edwards, 1995). This, together with lower water fluxes under the trees due to interception loss, creates a drier soil which can lead to increased soil N mineralisation compared to the moorland. Enhanced N

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deposition to the trees is also a possibility (e.g. Chapman et al., 1999; Neal, 2002; Soulsby et al., 2002).

Between 1994 and 2003, streamwater NO_3 concentrations increased at the Lower Hafren site, (Fig. 6), but not at the Upper. This was likely linked to the clear felling of some forest blocks in the lower catchment (Neal et al., 2004b). Previous work within the Plynlimon catchment has demonstrated that clear felling results in large increases in streamwater NO_3 concentrations and fluxes from the clear-felled block (Neal et al., 2003, 2004b, 2011, 2005; Reynolds and Edwards, 1995). After clear felling, the forest is re-planted, or less usually allowed to regenerate naturally. This creates a sink for N due to uptake by the actively-growing trees. The Hafren Forest as a whole is a patchwork of mature forest, clear-felled areas and rapidly growing young forest, thus limiting the observed increases in stream NO_3 due to clear felling. For instance, stream NO_3 concentrations in clear felled blocks at Plynlimon reached $4.3\,mg\,N\,L^{-1}$ (Neal et al., 2004b), whereas the average increase in Fig. 6 is $< 0.1\,mg\,N\,L^{-1}$. Whether the Upper or Lower Hafren has higher NO_3 concentrations depends on the balance between clear-felled and actively growing areas. The main felling years in the catchment were 1981, 1986, 1988, and 1994–1998 (Neal et al., 2004b) and there has been no significant felling since 2004. This pattern can be seen in Fig. 4. Nitrogen mineralisation after clear cutting also explains why previous research did not identify a significant trend in the Hafren streamwater NO_3 time-series, as the period analysed only covered 1988 to 2000/2002, the period over which the main felling years occurred (Evans and Monteith, 2001; Wright et al., 2001). These contrasting findings also raise questions over whether the twenty year time-series used in this research are of a sufficient length to accurately identify nutrient trends (Bernal et al., 2012). This question can only be answered by the continuation of monitoring in the Hafren system.

5.2 Controls on seasonal NO_3 dynamics

The seasonality in NO_3 time-series was consistent in both the Upper and Lower Hafren, with concentration peaks in the winter and minimums in the summer. Over the long-term study period, the phase of the seasonal NO_3 cycle was consistent, with annual minimums identified to occur in July for 90 % of the record. This annual minimum in July is coincident with annual minimums in streamflow and, with annual maximums in solar radiation and temperature. Solar radiation and temperature both affect biological activity, including N uptake processes in both the catchment and the stream. These two possibilities cannot be distinguished as causes of seasonal variation from these data. The diurnal variation appears to be due to instream processes (see below). However, the amplitude of the seasonal NO_3 variation is much greater than that of the diurnal variation (c. 0.2 mg N L^{-1} compared to 0.02–0.04 mg N L^{-1}; Figs. 6 and 8, Tables 5 and 6) whereas the amplitude of the temperature driver is only about double in seasonal cycles compared to diurnal cycles (Tables 5 and 6). It seems likely therefore that instream processes alone cannot account for the seasonal variation, though they will make a contribution – for instance studies in agricultural catchments tend to show higher instream NO_3 removal rates in summer (Birgand et al., 2007). The catchment is thus absorbing NO_3 more efficiently in summer – it is noticeable in Fig. 6 that unusually high NO_3 concentrations in the Upper Hafren occur exclusively in winter, though this is not so in the Lower Hafren during periods of clear felling. The results imply that N uptake processes appear to dominate over N production processes such as soil organic matter mineralisation, which would also be expected to increase in summer due to higher temperatures.

Figure 6 also shows an effect that is hard to explain other than by a decline in atmospheric N deposition – in the Upper Hafren the annual maximum NO_3 concentrations show a steady decline. These occur in winter when all the evidence suggests that biological uptake is small.

5.3 Controls on diurnal NO_3 dynamics: Spring 2007

Both the Upper and Lower Hafren show a single peak diurnal cycle in NO_3 concentrations which is strongest in summer and declines in winter (Figs. 8 and 9; Halliday et al., 2012). In the Upper Hafren this cycle had a consistent phase controlled by instream

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N uptake processes, however in the Lower Hafren the cycling was more complex with a variable phase and weaker amplitude, as a result of signal advection from the upstream site and changes in the catchment NO_3 processing in the forested reaches (see below).

5.3.1 Upper Hafren controls

The regularity of the cycle phase at Upper Hafren is consistent with the hypothesis that instream processing is responsible for the observed diurnal dynamics (Halliday et al., 2012). If the diurnal cycling was being controlled by catchment processes outside of the stream, more variability in the phase and amplitude of the diurnal dynamics would be anticipated as the signal observed in the stream would be the composite signal from across the whole catchment. In addition, the cycling would be expected to vary with flow, whereas as Fig. 8a, c show, the phase remains independent of flow over a wide range of conditions.

Possible causes for the diurnal cycle include N uptake by stream organisms and denitrification, driven by diurnal cycles of temperature and light flux. Both these correlate negatively with NO_3 concentration (Table 3), but the negative correlation is stronger with temperature than solar radiation. Partial correlation analysis showed that in the long-term datasets, temperature and solar radiation had independent effects on NO_3 concentration, but that temperature independent of solar radiation correlated better with NO_3 concentration. In the high frequency datasets, negative correlations with temperature alone remained high, but correlations with solar radiation independent of temperature were lower, and were not significant or even positive in the Lower Hafren (Table 7). Minimum NO_3 concentrations coincided with maximum diurnal air temperatures and lagged maximum solar radiation by approximately 2 h. Lag effects were investigated with solar radiation but no improvement in correlation was found. The long-term records from the Hafren demonstrated that the streamwater temperature difference between the upstream and downstream monitoring sites rarely exceeded 2 °C (< 8 % of the record). Therefore, changes in streamwater temperature along the river are unlikely to be critical in the differences observed in the diurnal system dynamics (Pattinson et al., 1998).

The correlation with solar radiation indicates a role for photosynthetic organisms in uptake, whereas the correlation with temperature could involve a variety of other organisms too. The Upper Hafren is a small oligotrophic stream which lacks significant macrophytes, and the streambed substrate consists largely of boulders, pebbles and exposed bedrock (Newson and Harrison, 1978). The most likely photosynthetic assimilators are the diatom biofilms and bryophytes growing on pebbles and rocks in the streambed (Fig. 1; see Sect. 2.1). Such biofilms are known to have strong NO_3 absorbing capacities (e.g. Duff et al., 2008), and this would explain the strong diurnal cycles with daytime minimums. This is also supported by the seasonal pattern in the observed diurnal dynamics, with the amplitude of the diurnal cycle strongest in the spring and summer periods and dying away to nothing during in the winter. Uptake would likely have been enhanced by the low flows and high temperatures experienced in the Spring 2007 period, as NO_3 removal is most efficient in small headwater streams at low flows due to the longer water residence times (Fig. 2; Dawson et al., 2001; Ranalli and Macalady, 2010). In addition, the higher NO_3 concentrations in the stream at this time, linked to the 2004–2006 drought (see Sect. 5.4), may also have enhanced biofilm growth during this period. The stronger correlation between NO_3 and temperature independent of solar radiation, indicates a role for non-photosynthetic organisms, perhaps in the deeper part of the hyporheic zone where uptake is not light-dependent (see review by Ranalli and Macalady, 2010). Denitrification or other removal processes in the hyporheic zone are a possibility (see Trimmer, 2012), even though this is a well-oxygenated system, but further research is required to determine the significance of this process to the diurnal streamwater NO_3 dynamics.

5.3.2 Lower Hafren controls

The change in the cycle phase between the upper and lower monitoring points fits with the hypothesis of advection of the NO_3 signal from the Upper Hafren monitoring point along the river. Using the discharge velocity relationships determined by Newson and Harris (1978), the travel time between the Upper and Lower Hafren was estimated to be approximately 2 h under normal flow conditions, less than an hour under stormflow conditions and over 7 h under baseflow conditions. Although these calculations were only an approximation of the travel time, they do indicate that the changes in cycle phase between the upper and lower monitoring points were consistent with the advection of the signal down the river – for instance the peak occurs 7 h later in low flow conditions in Fig. 8. Significant negative correlations were identified between the difference in timing of the diurnal NO_3 peaks between upper and lower monitoring point and the observed mean daily flow recorded at both sites ($\rho = -0.94$; $p < 0.001$; $N = 60$, and $\rho = -0.86$; $p < 0.001$; $N = 60$, for the Upper and Lower flows respectively). This result confirms that, as flow increases, the time required for signal advection downstream decreases.

The fact that the diurnal cycle at the Lower Hafren site appears to be dominated by the signal from the open moorland even though this is only about half the full catchment area (Fig. 1) shows that the forested area, which is a mixture of first and second-generation forest, does not have a consistent diurnal cycle of its own. Diurnal NO_3 cycling in the lower reaches may be reduced due to limited light penetration through the forest canopy to the stream reducing photosynthetic NO_3 uptake (Fig. 1; Dawson et al., 2001; Nimick et al., 2011; Rusjan et al., 2008; Rusjan and Mikos, 2010). The weaker cycling in the Lower Hafren may in part be driven by a "masking" of the diurnal variation as a result of the increased flow magnitude and variability at this monitoring point (Spring 2007: $Haf_{Low} = 2.507 \times (Haf_{Up}) - 0.036$; $r^2 = 0.94$; $p < 0.001$; $N = 5825$). These higher flows may have scoured the streambed rock surfaces in the lower reach, thus removing the diatom biofilms and bryophytes responsible for the diurnal NO_3 cycling at the Upper Hafren site (Chapman et al., 1996; Dawson and Wilby, 2001).

On the other hand, the lower NO_3 concentrations visible at low flow at the Lower Hafren site in the Spring 2007 period (Fig. 8) may be due to N uptake by the growing forest as discussed above, or by faster N processing in the forested catchment

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streams. For instance, in Spring 2007 the mean DOC concentration in the streamwater was 1.5 mg C L^{-1} at the Lower Hafren compared to 1.0 mg C L^{-1} at the Upper Hafren. Bernhardt and Likens (2002) showed that DOC enrichment in the stream draining Watershed 6 in the Hubbard Brook Experimental Forest New Hampshire, USA, stimulated microbial growth. The result also supports the hypothesis that the long-term decline in stream NO_3 is influenced by the long-term increase in DOC concentrations.

5.3.3 Significance of diurnal cycling

It is interesting to consider the significance of the diurnal variation in NO_3 concentrations compared to catchment N metabolism. If the diurnal amplitude on a particular day is taken as an estimate of N uptake (it may be an underestimate, because non-photosynthetic N uptake may still be occurring at the maximum amplitude), it is possible to estimate roughly how significant stream processing is in terms of catchment N metabolism. During the 8 days of maximum amplitude in Fig. 8 beginning 14 April 2007, the mean daily N uptake at the Upper Hafren site implied by the diurnal variation was about 0.14 kg N d^{-1}. On a stream area basis this amounts to approximately 180 mg N m^{-2} d^{-1}, assuming the Upper Hafren stream width is approximately 60 cm and length 1.3 km. This rate is comparable with values for streams in the Hubbard Brook Experimental forest (Bernhardt et al., 2002). Referred to the Upper Hafren catchment area (122 ha), this amounts to only 0.41 kg N ha^{-1} yr^{-1}. This is much smaller than the annual N retention by the Hafren catchment as a whole of approximately 14 kg N ha^{-1} yr^{-1} (e.g. Curtis et al., 2005), demonstrating that the terrestrial catchment still retains most of the N. The fate of the absorbed N is not known – it could be transferred higher in the food chain (e.g. to grazers on the biofilms) exported as particulate organic N or as gaseous N products, or retained in the sediments.

5.4 Temporal variability in diurnal NO_3 dynamics: the role of changingmeteorological conditions

During Spring 2008 the diurnal NO_3 cycle was much weaker and the phase of the cycle was much more variable than the dynamics observed in Spring 2007. The variability in the diurnal NO_3 dynamics between the years demonstrates how diurnal dynamics can be affected by both antecedent catchment conditions and meteorological events, such as droughts.

Water from the upper soil horizons acted as a source of NO_3 to the stream in both the Upper and Lower Hafren in Spring 2007. There were higher NO_3 concentrations at the Upper Hafren in Spring 2007, compared to Spring 2008, which may be the residual effect of NO_3 mineralised from the upper soil horizons after the end of the 2006 drought. As stated previously, Plynlimon experienced prolonged drought conditions between 2004 and 2006, which was then followed by one of the wettest summers on record, resulting in significantly elevated flow within the Hafren catchment in July 2007 (Fig. 2, see Sect. 2.2). Although mineralisation is limited by moisture stress during drought conditions, increased soil water NO_3 concentrations can occur as a result of increased evapotranspiration and reduced NO_3 uptake by drought-stressed vegetation (Reynolds and Edwards, 1995). Large amounts of NO_3 can then be leached into the stream in the immediate post-drought period as a consequence of mineralisation stimulation on re-wetting (Reynolds and Edwards, 1995). This effect was evident in the long-term dataset. Sharp peaks in NO_3 concentrations were observed in both the Upper and Lower Hafren NO_3 time series in the winter of 1996–1997 associated with the termination of the 1995–1996 drought, with similar peaks, although not as pronounced, in the winter of 2006–2007 (Fig. 4). In Spring 2007, there was a positive relationship between NO_3 and flow and between NO_3 and other soil water-derived determinands, Al and DOC, meaning that when a higher proportion of streamwater derived from upper soil horizons, NO_3 concentrations increased. Although the streamwater NO_3 data between June and July 2007 are limited in number due to a monitoring equipment malfunction, it is likely that the elevated flows experienced over this time resulted in a flushing of NO_3 from the enriched soils into the streamwater (Reynolds and Edwards, 1995), such that by 2008 the soils' NO_3 concentrations had returned to pre-drought levels. Consequently, there was reduced NO_3 available for delivery to the stream in Spring 2008, in comparison to Spring 2007, and thus NO_3 concentrations were lower.

Other factors may also have contributed to the weaker and more variable diurnal NO_3 cycling in Spring 2008 compared to Spring 2007. The mean flow was considerably higher ($0.10\,m^3\,s^{-1}$, compared to $0.06\,m^3\,s^{-1}$). This may have removed some diatom biofilms from the rock surfaces, and diatoms are the organisms probably mainly responsible for the observed diurnal NO_3 cycling (e.g. Chapman et al., 1996; Dawson and Wilby, 2001). In addition, temperatures were also significantly lower in 2008 (mean temperature of 3.6 °C compared to 6.4 °C). Consequently, biological activity is likely to have been lower in 2008 reducing the diurnal NO_3 dynamic amplitude.

The impact of drought conditions on the diurnal NO_3 cycle has important implications when considering the impact of future climate variability on catchment NO_3 dynamics. The analysis of the 2007 and 2008 data suggests that extreme meteorological events, the frequency of which are predicted to increase the UK (Marsh et al., 2007), can result in enhanced diurnal cycling of NO_3, with maximum amplitude of the diurnal cycle over two times higher in Spring 2007 compared to Spring 2008, and consequently cause these short-term dynamics to form a stronger component of the complete NO_3 time series. The interpretation of short-term data series needs caution if there are no long-term data to put them in context.

6 Conclusions

There is no clear evidence that the long term declining trends in streamwater NO_3 concentrations are driven by declining atmospheric N deposition alone, with the initial increasing trend in atmospheric deposition not reflected in the streamwater NO_3 concentrations. This is consistent with findings in other systems where declining streamwa-

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ter NO_3 trends do not follow deposition (see e.g. Goodale et al., 2003; Bernhardt et al., 2005; Bernal et al., 2012), but are instead linked to features such as recovery from catchment disturbance and presence of organic debris dams. In the Hafren, increased N uptake caused by increasing temperatures and increased denitrification stimulated by increasing streamwater DOC concentrations have been identified as possible contributory factors in the declining streamwater NO_3 concentrations. Further work is needed to fully understand the mechanisms controlling the coupling of C and N in this river-system. The seasonality in the streamwater NO_3 time-series was linked to flow and catchment biological activity and this now seems well established as a general rule for a majority of catchments. The diurnal NO_3 cycling in the Upper Hafren was controlled by instream autotrophic assimilation, with the dynamics at the Lower Hafren a composite of the advected signal from the upstream site and changes in NO_3 processing in the forested reaches of the catchment. The importance of autotrophic NO_3 uptake on diurnal variations in streamwater NO_3 concentrations has also been noted in other studies (Mulholland et al., 2006). In upland systems with limited anthropogenic influences this type of diurnal NO_3 cycle is likely to form a key component of the streamwater NO_3 dynamics. Therefore these diurnal dynamics should be considered when designing a low-frequency sampling programmes, as the time of day at which the samples are collected will affect the NO_3 concentration determined, and could subsequently impact on any conclusions drawn about the system. The enhanced diurnal NO_3 cycling observed in the catchment in 2007, as a result of the optimal conditions – high temperatures, low flows and increased NO_3 availability – in the post drought period, has implications when considering the importance of diurnal NO_3 variations to the overall NO_3 cycle under future climate projections.

Full validation of the statistically modelled dynamics requires hourly measurements to ensure that the diurnal peaks and minimums were captured. However, high-frequency monitoring is extremely expensive. Given the climatic variability experienced in the UK, this poses challenges, as with only short-term monitoring is it difficult to determine whether the observed diurnal dynamics are "normal" or "atypical". Work deploying in situ UV spectrophotometers has demonstrated that such instruments provide extremely reliable NO_3 measurements for a range of different catchments and climatic settings (Chapin et al., 2004; Johnson et al., 2006; Sakamoto et al., 2009; Wade et al., 2012; Zielinski et al., 2011), and could provide the answer for robust long-term high-frequency NO_3 monitoring at Plynlimon and elsewhere. The importance of studying all nutrient fractions, in particular the organic fraction, should not be overlooked (e.g. Durand et al., 2011). Where it was possible to study different N fractions in the Hafren system, as the samples were returned to the laboratory for analysis, in situ instruments are currently only available for specific determinands. In addition, automated in situ sample filtration remains a challenge (Wade et al., 2012). Therefore, researchers need to consider the value of high-frequency data, without information on all nutrient fractions.

Data availability/resolution has been recognised as one of the main limitation of hydrochemical studies (e.g. Bouwman et al., 2013; Kirchner et al., 2004). This study demonstrates that long-term water quality data are needed to put the short-term, high-frequency data into context, and to identify the role of both gradually-changing influences and sporadic rare events such as droughts. The combination of the two monitoring approaches allows hypotheses about the controls on stream NO_3 dynamics to be tested more rigorously, and for new research questions to be generated. Together the long-term and high-frequency data allow inferences about underlying processes controlling the observed NO_3 dynamics to be made – for instance at Plynlimon the seasonal NO_3 trends show that declining atmospheric N deposition is having an effect, with successive smaller seasonal NO_3 maximums, and the diurnal variations show the influence of instream processing, demonstrating that the river is not simply a conduit. Without associated environmental data, such as discharge, rainfall and meteorological data, it would have been impossible to elucidate the principal mechanisms operating within the Hafren system. Therefore, there is a need to think pragmatically about monitoring, as the value of the high-frequency data is determined by the system understanding it can provide. Researchers have to ask themselves how much they will really

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be able to learn about the system from only a short period of intensive monitoring. Instead researchers should consider undertaking high-frequency monitoring in catchments with already well-established monitoring networks, such as Plynlimon, where the high-frequency data can be best interpreted. The continued and more widespread collection of high resolution NO_3 data from a variety of catchments will further enhance our understanding of watershed dynamics and allow the quantification of the importance of diurnal cycling and the role of instream processing.

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Table 1. Plynlimon monitoring programme details.

Monitoring Point	Type of Monitoring	Frequency	Duration	Start	End
Carreg Wen	Cloud water volume and quality	Weekly	21 yr	25 Sep 1990	Ongoing
	Rainfall water volume	Weekly	28 yr	10 May 1983	Ongoing
	and quality	7-hourly	1.9 yr	6 Mar 2007	27 Jan 2009
	Air temperature	Hourly	36 yr	3 Jan 1976	Ongoing
	Incoming solar radiation				
Upper Hafren	Streamwater quality	Weekly	21 yr	17 Jul 1990	Ongoing
		7-hourly	1.9 yr	6 Mar 2007	27 Jan 2009
	Flow	15 min	6 yr	3 Feb 2005	Ongoing
Lower Hafren	Streamwater quality	Weekly	28 yr	10 May 1983	Ongoing
		7-hourly	1 yr	6 Mar 2007	11 Mar 2008
	Flow	15 min	36 yr	1 Jan 1976	Ongoing

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Table 2. Summary statistics for the Plynlimon NO_3 time-series ($mg\,N\,L^{-1}$): all statistics were based on the complete NO_3 record for each site, and Spring 2007 statistics are based on high-frequency data.

Summary Statistics	Long-term				High-frequency			Spring 2007	
	Upper	Lower	Rainfall	Cloud	Upper	Lower	Rainfall	Upper	Lower
No. Data Points	1009	1376	1031	793	2056	896	842	201	189
Minimum	0.01	0.02	< 0.01	0.05	0.01	0.02	0.01	0.02	0.02
Max	1.03	1.35	2.89	49.68	0.37	0.34	3.88	0.23	0.28
Range	1.02	1.33	2.89	49.63	0.36	0.33	3.88	0.21	0.26
3rd Quartile	0.25	0.33	0.30	4.52	0.19	0.20	0.24	0.19	0.17
1st Quartile	0.12	0.17	0.09	0.76	0.11	0.10	0.07	0.14	0.08
Interquartile range	0.12	0.16	0.21	3.76	0.08	0.10	0.17	0.05	0.09
Mean	0.19	0.26	0.28	4.01	0.15	0.15	0.26	0.16	0.12
Median	0.17	0.24	0.15	1.93	0.15	0.16	0.12	0.17	0.12
Stormflow mean	0.19	0.31	–	–	0.13	0.19	–	0.19	0.19
Baseflow mean	0.15	0.16	–	–	0.14	0.08	–	0.15	0.06
Flow weighted mean	0.19	0.28	–	–	0.12	0.13	–	0.16	0.13
99th Percentile	0.49	0.63	1.98	29.42	0.30	0.28	2.39	0.21	0.26
1st Percentile	0.05	0.07	0.03	0.17	0.05	0.04	0.02	0.06	0.03
Variance	0.01	0.02	0.14	33.50	0.00	0.00	0.19	0.00	0.00
Standard deviation	0.09	0.12	0.37	5.79	0.06	0.06	0.44	0.04	0.05
Coefficient of variation	48	48	132	144	37	40	169	23	43

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Table 3. Spearman's rank correlation coefficients (ρ) between NO_3 and a selection of other determinands recorded at the upper and lower Hafren sites over various time periods.

Determinand	Upper			Lower	
	Long-term	Spring 2007	Spring 2008	Long-term	Spring 2007
Flow	0.19[a]	0.71[a]	0.06	0.46[a]	0.87[a]
pH	−0.28[a]	−0.69[a]	−0.24[b]	−0.59[a]	−0.83[a]
Alkalinity	−0.40[a]	−0.65[a]	−0.14	−0.60[a]	−0.81[a]
Conductivity	0.37[a]	–	–	0.53[a]	–
Calcium	−0.07	−0.58[a]	−0.07	−0.10[a]	−0.52[a]
Magnesium	0.24[a]	−0.43[a]	0.07	0.28[a]	0.05
Aluminium	0.03	0.67[a]	0.01	0.56[a]	0.82[a]
Dissolved Organic Carbon	−0.33[a]	0.58[a]	−0.18	−0.11[a]	0.39[a]
Chloride	0.34[a]	–	0.55[a]	0.32[a]	–
Sodium	0.20[a]	−0.42[a]	–	0.23[a]	0.40[a]
Manganese	0.40[a]	0.71[a]	0.24[b]	0.66[a]	0.86[a]
Cobalt	0.41[a]	0.75[a]	0.72[a]	0.67[a]	0.85[a]
Arsenic	−0.59[a]	−0.68[a]	0.58[a]	−0.34[a]	−0.70[a]
Silicon	0.10[b]	–	−0.49[a]	−0.24[a]	–
Cerium	−0.08	0.63[a]	–	0.28[a]	0.77[a]
Praseodymium	−0.09	0.68[a]	−0.07	0.23[a]	0.77[a]
Streamwater Temperature	−0.77[a]	–	–	−0.60[a]	–
Air Temperature[c]	−0.72[a]	−0.78[a]	−0.56[a]	−0.61[a]	−0.58[a]
Solar Radiation[c]	−0.50[a]	−0.43[a]	−0.33[a]	−0.50[a]	−0.07

[a] Correlation statistically significant at $p < 0.001$;
[b] $p < 0.01$.
[c] Recorded at the Carreg Wen Automatic Weather Station.
– data unavailable

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Table 4. The median difference in concentration between the lower and upper monitoring points for the complete time-series and the baseflow and stormflow periods[a].

Monitoring Programme	Complete Datasets	Baseflow	Stormflow
High-frequency	$-0.02^{b(865)}$	$-0.06^{b(105)}$	$0.03^{b(86)}$
Long-term	$0.03^{b(1005)}$	$0.00^{c(85)}$	$0.07^{b(107)}$
Long-term (2007)[d]	$-0.01^{c(50)}$	$-0.01^{(6)}$	$0.02^{(7)}$

[a] Results of the one-sample Wilcoxon signed rank test: significantly different from zero at $p < 0.001^{b}$; $p < 0.05^{c}$ (Number of samples in brackets).
[d] Annual concentration difference for the year 2007 based on the long-term monitoring.

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Table 5. Seasonality Analysis: the results of the DHR seasonal cycle extracted from the long-term streamwater NO_3, flow and temperature time-series at both sites and from the rainfall NO_3, air temperature and incoming solar radiation time-series recorded at Carreg Wen Automatic Weather Station.

Site	Determinand	Dominant Phase Peak	Dominant Phase Minima	Maximum Annual Amplitude	Average Strength*	Seasonality Amplitude Trend
Upper Hafren	NO_3	Jan	Jul	$0.23\,mg\,N\,L^{-1}$	62 %	Decreasing throughout the period of record
	Flow	Dec	Jun	$0.11\,m^3\,s^{-1}$	17 %	Variable
	Streamwater Temp.	Jul	Jan	7.05 °C	66 %	Decreasing amplitude until 1999 and increasing since
Lower Hafren	NO_3	Jan	Jul	$0.24\,mg\,N\,L^{-1}$	57 %	Overall decrease over the period of record, with a period of increasing amplitude between 1993 and 1998
	Flow	Jan	Jul	$0.28\,m^3\,s^{-1}$	18 %	Variable
	Streamwater Temp.	Aug	Feb	8.27 °C	59 %	Increasing throughout the period of record
Carreg Wen	Air Temp.	Jul	Jan	13.2 °C	55 %	Decreasing between 1984 and 1998 and increasing since
	Solar Radiation	Jun	Dec	$444\,W\,m^{-2}$	55 %	Decreasing between 1984 and 1996 and increasing since

* The average strength of the seasonal cycle has been calculated as the average percentage of annual variability (the range of concentrations recorded) explained by the maximum amplitude of the identified annual cycle.

Table 6. Diurnal Cycle Analysis: the results of the diurnal cycle extracted from the high-frequency NO_3 time-series using Dynamic Harmonic Regression. Diurnal cycling within the air temperature and solar radiation time-series was also investigated.

Monitoring Point	Determinand	Spring Period	Dominant Peak Time (GMT)	Dominant Minimum Time (GMT)	Maximum diurnal cycle amplitude	Average diurnal cycle amplitude	Percentage of diurnal variability*
Upper Hafren	NO_3 (mg N L^{-1})	2007	02:00–03:00	14:00–15:00	0.07	0.04	80 %
		2008	00:00–01:00	12:00–13:00	0.03	0.02	58 %
Lower Hafren	NO_3 (mg N L^{-1})	2007	09:00	21:00	0.05	0.04	76 %
Carreg Wen	Air Temp. (°C)	2007	14:00–15:00	02:00–03:00	12.7	6.07	83 %
		2008	14:00–15:00	23:00–01:00	9.12	3.79	79 %
	Solar Radiation (W m^{-2})	2007	12:00	Zero between 18:00–05:00	456	285	42 %
		2008	11:00–13:00	Zero between 18:00–05:00	469	205	40 %

* The percentage of diurnal variability has been calculated as the average percentage of daily variability (i.e. the range of concentrations recorded on a given day) explained by the maximum amplitude of the identified diurnal cycle on the same day.

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Table 7. Partial Correlation Analysis – Investigation of the NO_3, Temperature and Solar Radiation relationship in the Hafren Catchment.

Determinand	Effect Eliminated	Long-term		High-frequency		Spring 2007		Spring 2008
		Upper	Lower	Upper	Lower	Upper	Lower	Upper
Temperature[a]	Solar Radiation	−0.69[b]	−0.48[b]	−0.60[b]	−0.66[b]	−0.72[b]	−0.64[b]	−0.55[b]
Solar Radiation[a]	Temperature	−0.17[b]	−0.32[b]	−0.11[b]	0.00	−0.09	0.33[b]	−0.15

[a] Streamwater temperature for the long-term data; air temperature for the high-frequency data and Spring periods.
[b] Correlation statistically significant at $p < 0.001$.

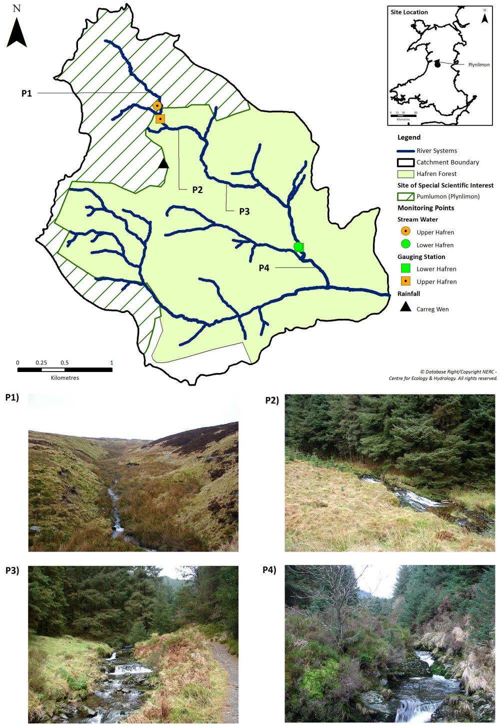

Fig. 1. Plynlimon catchment study area (Brandt et al., 2004). Photographs of the Hafren catchment taken on the 15 January 2009 by John Lucas and licensed for reuse under this Creative Commons Licence: **(P1)** the River Hafren upstream of the Upper Hafren monitoring point, picture looks upstream towards the source of the river (SN827893), **(P2)** the River Hafren downstream of the Upper Hafren Flume (SN828889), **(P3)** the River Hafren within the Hafren forest, picture looks upstream towards the steep valley of Graig Wen (SN835883), **(P4)** the Severn downstream of the Hafren Flume, picture looks upstream from a footbridge over the river (SN844874).

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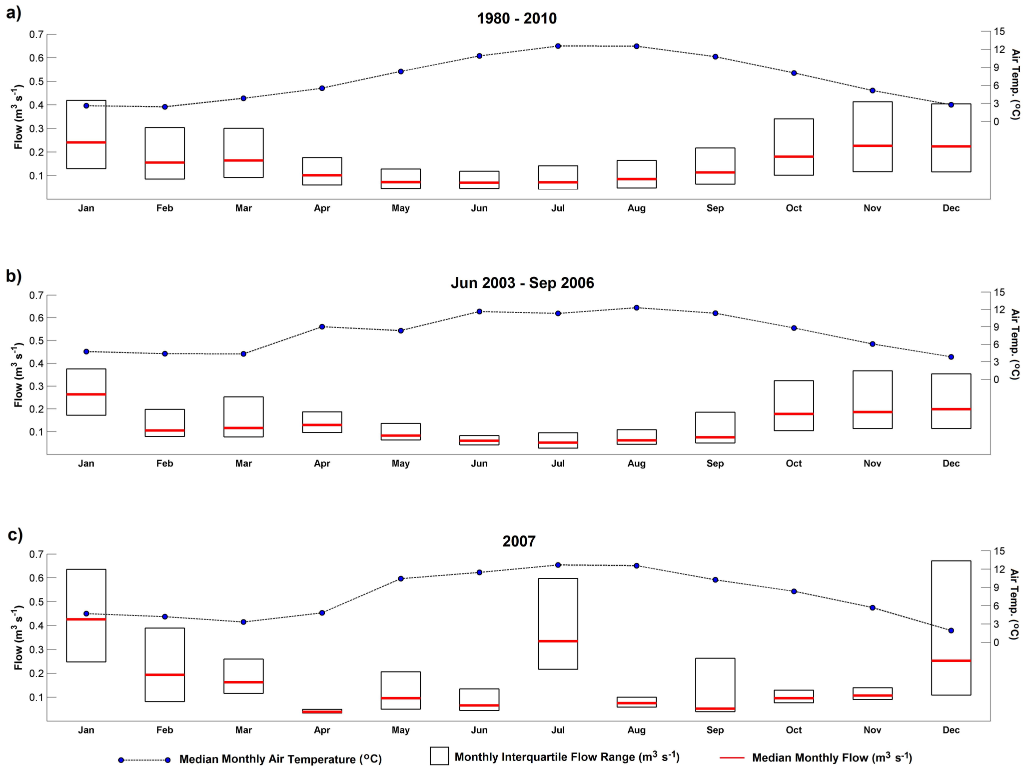

Fig. 2. Seasonal flow and air temperature patterns for the Hafren catchment, with the interquartile range and median flow for each month based on the 15 min flow record recorded at the Lower Hafren gauging station, and the median air temperature for each month based on the hourly temperature record recorded at Carreg Wen AWS shown: **(a)** long-term average, 1980–2010, **(b)** average conditions during the 2003–06 drought, June 2003–September 2006, **(c)** conditions during the first year of the high-frequency monitoring scheme, 2007.

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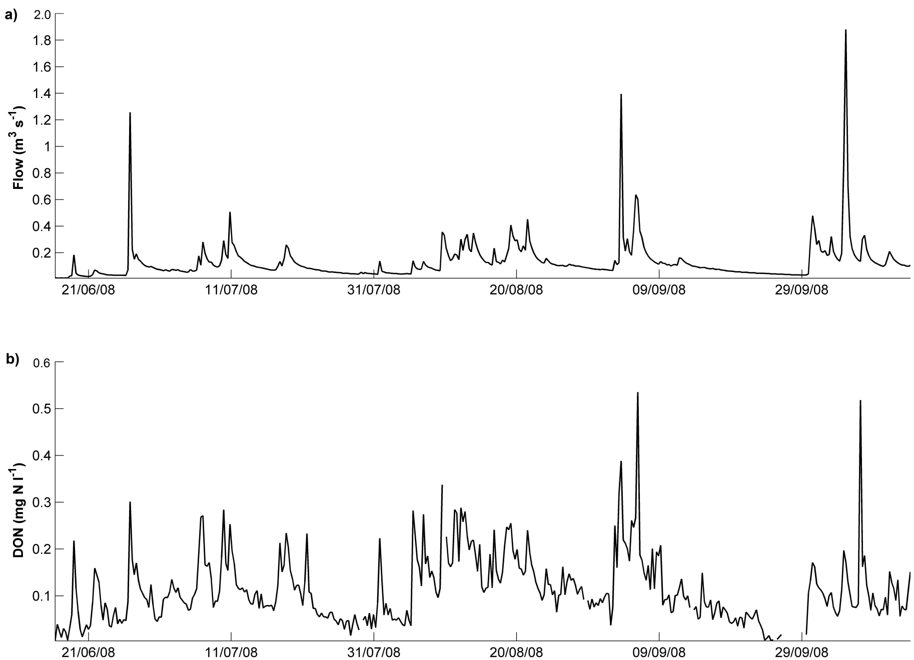

Fig. 3. Extract of the high-frequency dissolved organic nitrogen (DON) time-series recorded at the Upper Hafren monitoring station between June and September 2008: **(a)** flow ($m^3\,s^{-1}$) and **(b)** DON ($mg\,N\,L^{-1}$).

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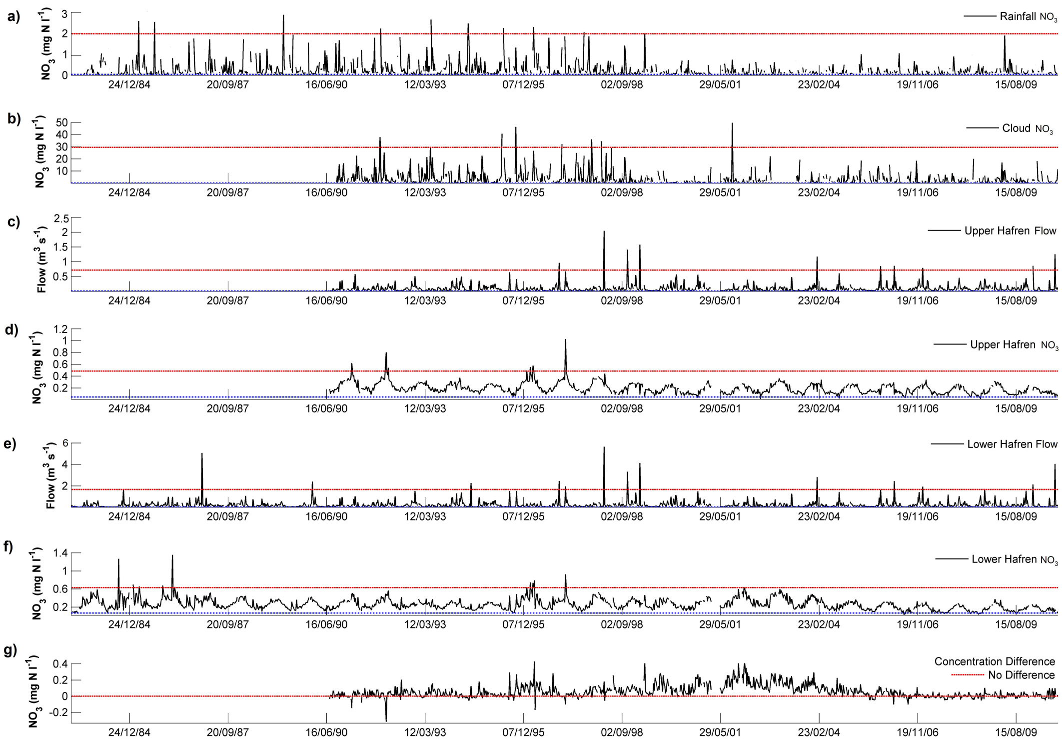

Fig. 4. Long-term NO_3 and flow time-series recorded within the Plynlimon catchment mid-Wales. The red line and the blue line on plots **(a–f)** represent the 99th and 1st percentile of the time-series respectively. Concentration difference plot, **(g)**, is based on the Lower Hafren NO_3 concentration minus the concentration recorded at the Upper Hafren for each time-step.

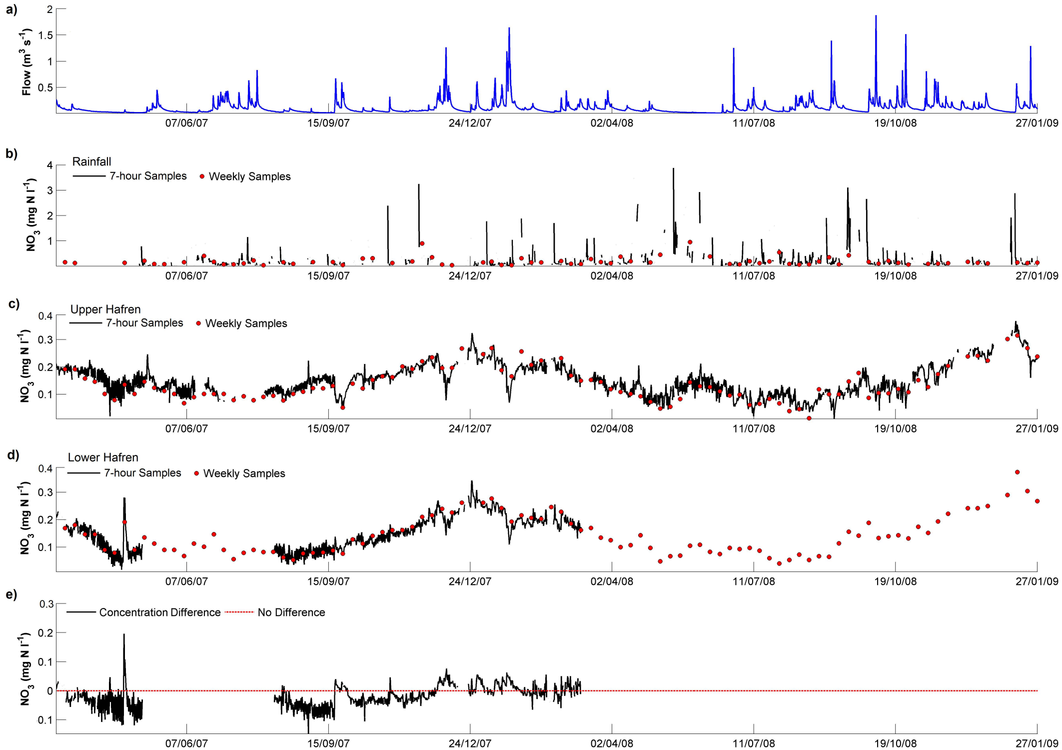

Fig. 5. High-frequency NO_3 time-series recorded within the Plynlimon catchment mid-Wales (7 h samples), with the long-term weekly monitoring samples overlain (Weekly samples). Concentration difference plot, **(e)**, is based on the Lower Hafren NO_3 concentration minus the concentration recorded at the Upper Hafren for each time-step.

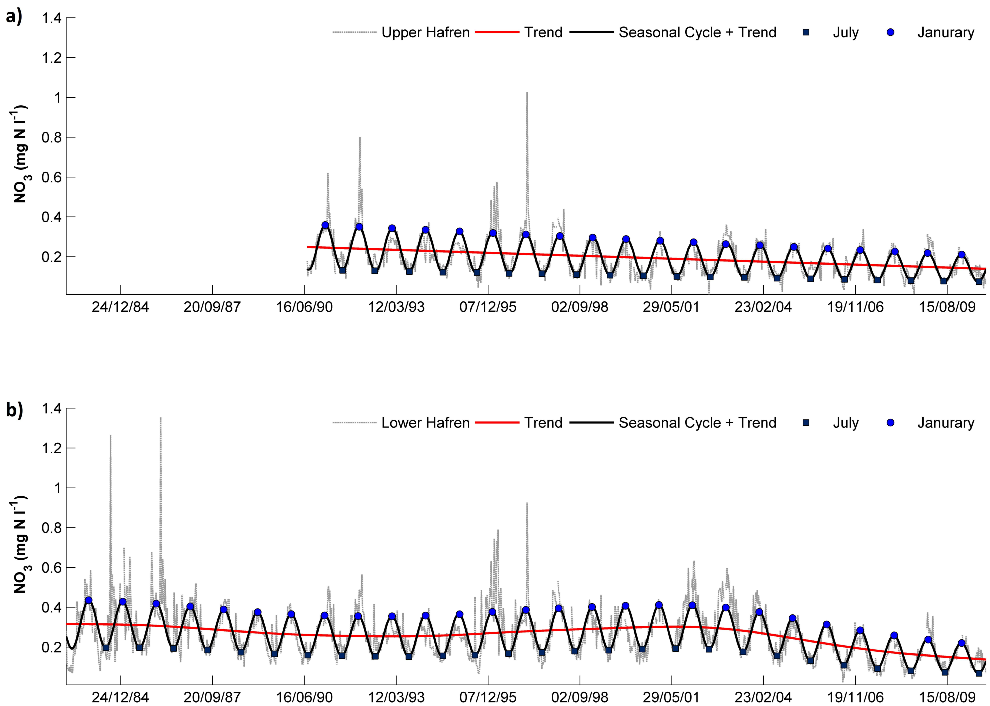

Fig. 6. Long-term NO_3 trends and seasonality within the Plynlimon NO_3 time-series: **(a)** Upper Hafren and **(b)** Lower Hafren. Trends and seasonal cycles have been established through DHR analysis of the low-frequency time-series using the CAPTAIN toolbox.

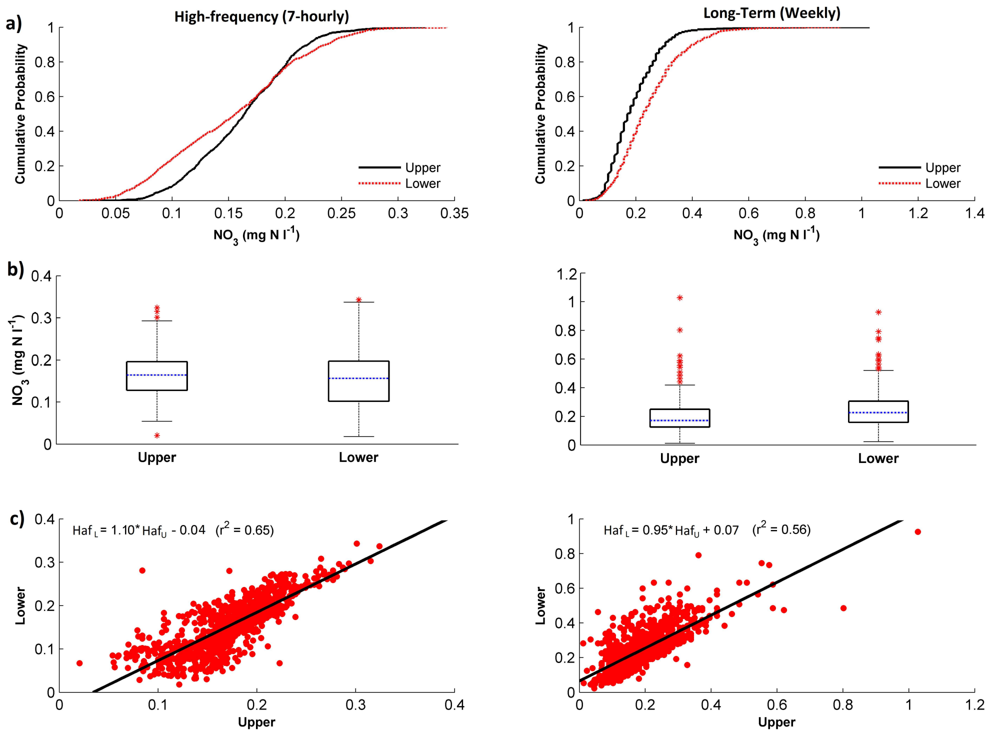

Fig. 7. NO_3 time-series distribution plots. Plots show the common period of record for each dataset long-term 1990–2010, high-frequency March 2007–March 2008: **(a)** distribution plots, **(b)** box plots where the box is the inter-quartile range (IRQ), the line across the box is the median, the whiskers are $\pm 1.5 \times$ IQR, and extremes, denoted *, are any points outside this range, and **(c)** relationships between the NO_3 concentrations at the Upper and Lower catchment monitoring locations. The left hand column displays the high-frequency data and the right the long-term data.

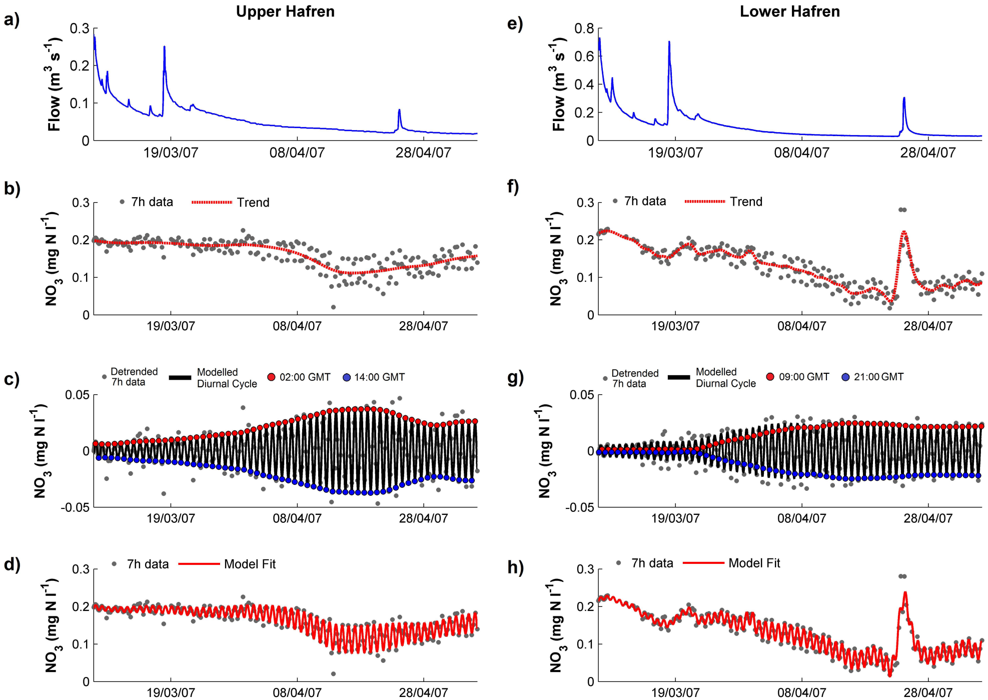

Fig. 8. Statistically modelled diurnal cycling within Spring 2007 (March to May 2007) of Hafren NO_3 time-series, using Dynamic Harmonic Regression. On the left hand-side are the Upper Hafren data and on the right hand-side the Lower Hafren: **(a, e)** flow, **(b, f)** modelled trend, with observed data, **(c, g)** modelled diurnal cycle, with detrended data and **(d, h)** model fit (trend + diurnal cycle), with observed data. Diurnal cycle plots show variations above and below the identified trend (zero).

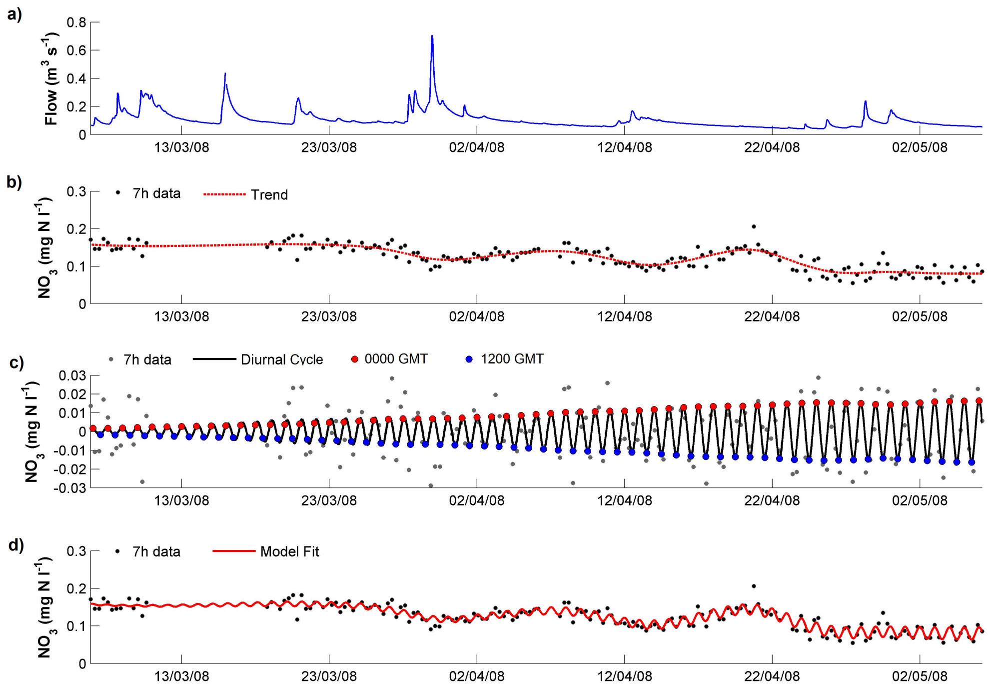

Fig. 9. Statistically modelled diurnal cycling within Spring 2008 (March to May 2008) of the Upper Hafren NO_3 time-series, using Dynamic Harmonic Regression: **(a)** flow, **(b)** modelled trend, with observed data, **(c)** modelled diurnal cycle, with detrended data and **(d)** model fit (trend + diurnal cycle), with observed data. Diurnal cycle plots show variations above and below the identified trend (zero).

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