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Interactive comment on "Upland streamwater nitrate dynamics across decadal to sub-daily timescales: a case study of Plynlimon, Wales" *by* S. J. Halliday et al.

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The authors would like to thank Dr Cohen and Dr Pellerin for their detailed and constructive comments on the manuscript. We are extremely pleased that both reviewers agreed that the manuscript makes a useful contribution to the literature.

Reviewer 1 – Matt Cohen (R1)

In this paper, the authors present and analyze an unprecedented data set on nitrate concentrations at two locations in the River Hafren. The data set consists of two time

series: one low resolution (weekly) extending over nearly 30 years, and a second shorter (ca. 2 years) but at much higher resolution (1 sample per 7 hours). The resulting dynamics are enormously illustrative about catchment and stream processes. The paper is well written and organized, and the analyses appear to be robust. While the paper is expertly crafted, I have some questions and comments about some interpretations.

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R1 Comment 1: Interpretations of nitrate declines: First, from the long term data set, there was a clear decline in N deposition followed some time later (ca. 5 years based on a visual analysis of Fig. 4) by a decline in streamwater NO3 concentrations. However, the authors assert that N deposition alone couldn't explain the declining trend in streamwater N export because the effects were not simultaneous (i.e., the streamwater decline lagged). I am not at all clear why we would expect an instantaneous response. The stream is a tiny fraction of the total catchment area, so most of the N deposition is terrestrial, and the terrestrial N cycle would presumably have some inertia (i.e., lags) wherein higher N leakage rates could persist for some time even after high N loading ceases. Indeed, the authors allude elsewhere (section 5.3.3) to the primacy of terrestrial N retention vis-à-vis stream retention, and given that N deposited to a supposedly N limited system wouldn't be immediately exported, it seems that a 5 year lag is wholly plausible. I wondered if this means that changes in N deposition may indeed be a sufficient explanation. I was also a little confused by the invocation of temperature variation as a partial explanation for the observed decline, and for both long term and short term temporal patterns.

Authors' Response: The authors agree that the catchment response to decreased N deposition would not be instantaneous. However, the point we wish to raise in the paper is that while N deposition was increasing throughout the first 15 years of record (1983 – 1997 in the rainfall record), this is not reflected at all in the Upper Hafren streamwater time-series, where a declining trend is identified throughout the period of record (1990 – 2011). If the trend was being controlled by deposition alone, and a lagged response was expected in the streamwater, we would have expected to see an increasing trend at least at the start of the study period. This is why the authors believe that although declining deposition will have clearly played a role in the declining streamwater N concentrations, additional processes are likely to have contributed to this. Some changes have been made to the text to demonstrate that we would not anticipate the deposition trend and streamwater trends to mirror one another exactly (Line 592), but in general we feel that the discussion section on the drivers of the long-term trend is clear.

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R1 Comment 2: Temperature data are presented only in tables from which it's very difficult to visualize the relevance of this apparently key variable. One suggestion is to jettison Fig. 3 (from which almost no inference is made) and replace this with presentations of stream and air temperature variation.

Authors' Response: Thank you for this suggestion. We agree that the manuscript would be improved by the removal of Figure 3 and its replacement with a figure showing the explanatory variables. This has now been done and is Figure 6. This is present at the end of the authors comments (under Figure 1) and the full figure caption is: Fig. 6 Explanatory variables: The left hand side is the complete record (1983 to 2010) and the right hand side is the period of record covering the high-frequency study period: a) Hourly flow at Lower Hafren gauging station, b) Hourly rainfall at Carreg Wen Automatic Weather Station (CW-AWS), c) Hourly solar Radiation at CW- AWS, and d) Hourly air temperature at CW-AWS and weekly streamwater temperature at the Lower Hafren monitoring point.

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R1 Comment 3: Controls on Diurnal Nitrate Variation: Second, considerable time is spent evaluating the controls on diurnal nitrate variation, and particularly the lag be-

hind solar radiation, but not air temperature (water temperature being unavailable because of the sampling protocol). The authors conclude that the correlation of nitrate concentration with air temperature, which is stronger than with solar radiation, suggests that autotrophic uptake alone can't explain the variation. This seems incorrect to me. Solar radiation would be expected to peak prior to the minima of the nitrate signal because of the time lags associated with stream advection. This is evident in the Rusjan and Mikos (2010) data set that the authors cite, and even more clearly in work by Heffernan and Cohen (2010; Limnology and Oceanography) that shows 3-4 hour lags between maximum solar radiation and peak NO3 retention (i.e., concentration minima). This corresponds to the time for water in the stream at peak irradiance to arrive at the downstream monitoring location (which is ca. half the residence time in a system with limited dispersion). In short, the expectation is for a lag in nitrate dynamics behind the primary driver of autotrophic uptake. The fact that this lag is roughly similar to the lag between peak radiation and air temperature (a lag induced by thermal mass of the air and land) may be circumstantial. In any event, while temperature increases would be expected to enhance denitrification and assimilation reaction rates, these are almost certainly counter-balanced by the inhibition of denitrification by produduction of photosynthetically derived dissolved oxygen (e.g., see Christensen et al. 1999 in Limnology and Oceanography and/or Harrison et al. 2005 in Aquatic Sciences for diurnal solute variation driven indirectly by DO availability).

Authors' Response: The authors do not conclude the stronger correlation with temperature over solar radiation means that autotrophic uptake alone can't explain the diurnal NO3 dynamics. Instead we simply outline that while autotrophic uptake is likely the principal driver of the observed diurnal dynamics, the possible role of denitrification in the hyporheic zone cannot be ruled out based on the available data. Lines 614 – 623 and Lines 736 – 742 recognise that denitrification in the streamwater will be highly unlikely in the Hafren system as it is extremely well oxygenated system. However this does not preclude the possibility that denitrification is taking place at microsites in the streambed or hyporheic zone. We have made some small changes to the text to reemphasize that we believe the diurnal cycling in the upper reaches is being driven autotrophic uptake.

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R1 Comment 4: Changes in Signals between Upper and Lower Stations: The translation of the upper Hafren signal to the lower Hafren station, with the lag time dependent on flow, was particularly interesting. The authors explain this by invoking that the weaker signal (which I interpreted to mean smaller amplitude) is due to scoured autotrophs and more shade; this seems plausible. However, absent any specific information about this, it seems prudent to consider another explanation: simply that the diurnal signal is attenuated because of the accumulating effects of dispersion. Assuming the diurnal signal is induced by autotrophs in the upper reach and then simply transported through the lower reach (where shade precludes additional diurnally varying uptake), the effects of dispersion and storage would necessarily dampen the signal. This effect would likely be lower at high flows because of shorter travel times (and therefore lower Peclet numbers). One attractive feature of this strictly hydraulic explanation is that it allows the inclusion of denitrification in the lower reaches as an explanation for reduced absolute concentration. In other words, dominant N removal pathways may be different between reaches (autotrophs in the upper, heterotrophs in the lower).

Authors' Response: "Weaker amplitude" did refer to "smaller" and this has been altered in the text to make this clear. The authors agree that the dispersion effect of increasing flow could alone explain the reduction in the amplitude of the diurnal NO3 dynamics at the lower Hafren site. However, again based on the available data, it is not possible to rule out additional contributory factors. The text in this section has been re-arranged to try and emphasize the role of dispersion.

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R1 Comment 5: Inferences about Diurnal Variation: Finally, I had two minor comments

on inferences made about diurnal variation. First, the estimates of retention on a per unit stream area due to autotrophs (likely the dominant factor inducing diurnal variation) are plausible, but very high. Heffernan and Cohen (2010 in Limnology and Oceanography) report N retention from diurnal integration of nitrate variation which corresponded strongly with primary production; their peak rates in an exceedingly productive subtropical river are roughly half the 180 mg N m-2 d-1 reported here. Is there any summertime primary production information available for these streams that would help bound this estimate (e.g., by providing an estimate of the implied C:N stoichiometry)? Bounding this number based on metabolism and autotroph stoichiometry is important because overlapping processes (e.g., diurnal variation induced by dynamic blending of source waters - see Pellerin et al. 2012 in Biogeochemistry) may amplify or dampen the signal, and confound attribution of diurnal variation to just one process.

Authors' Response: Here we were attempting to demonstrate that in-stream uptake was small compared to catchment uptake by using maximal values for the latter. Heffernan and Cohen (2010) use a more sophisticated method to estimate N uptake, though the principle is the same, in that they take the integral of the diel NO3 depletion curve whereas we were just using the maximum daily depletion. Their value will thus be lower (and more accurate). To make our results comparable, we have re-calculated using one of the methods in the Heffernan and Cohen paper (Equation 6, line 799 in Section 5.3.3). This brings the value down below that of their system, and makes our point even more strongly. We would not wish to make too much of the exact figures, as with such a narrow stream there is a large error on streambed area. Unfortunately, there are no primary production or DO data to enable us to put bounds on these estimates.

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R1 Comment 6: Second, the authors interpret the lower variation in spring 2008 as evidence of temperature differences (which are modest) and scour of aquatic autotrophs (from which they would presumably recover fairly quickly; see Biggs 2000 in JNABS and Fisher et al. 1982 in Ecological Monographs). I would submit that the most parsimonious explanation for the reduced amplitude is higher flow. The flows in 2008 are roughly double those in 2007, and the diurnal NO3 amplitude in 2008 is roughly half that in 2007. Assuming the benthic area doesn't change much with changing flow (i.e., most of the change is in depth, not width), the reduced amplitude simply reflects the greater mass of water (and thus nitrate) on which the benthic uptake process is acting. This would, in my view, affect the inference about the impacts of changing climate.

Authors' Response: The authors believe the drought conditions which proceeded the 2007 monitoring period are key to the enhanced diurnal NO3 dynamics observed during this Spring period. The focus of the paragraph has thus been shifted to demonstrate that it was the reduced flow and higher temperatures in combination with the greater availability of NO3 which led to the larger more consistent dynamics observed in 2007.

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R1 Comment 7: In spite of some quibbles with the interpretations, I reiterate that this is an important paper and dataset from which important lessons and insights are drawn. Moreover, this study sets demonstrates the importance of long-term and high-resolution solute monitoring for drawing inferences about biogeochemical processes and environmental change.

Authors' Response: The authors greatly appreciate Dr Cohen's positive comments on the manuscript.

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Reviewer 2 – Brian Pellerin (R2)

The manuscript by Halliday et al. (Upland streamwater nitrate dynamics across decadal to sub-daily timescales: a case study of Plynlimon, Wales) describes a long-term time series of nitrate concentrations at two locations with different land cover in Wales. The study demonstrates long-term trends in nitrate concentrations relative to

potential drivers including atmospheric deposition and temperature, and explores possible explanations for seasonal and diurnal variability. The dataset is important and the paper is significant, both for the interpretation of broad scale patterns but also as a way to move forward time series analysis of water quality data in freshwater systems. Specific Comments: The data quality and analysis seems technically sound. I only have a few comments.

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R2 Comment 1: I appreciate that you were clear about the implications of 7 hr sampling intervals on interpreting diurnal patterns. I'm fine with your approach to model the hourly values, but think the broader community would benefit from a more detailed description of the DHR approach that you used.

Authors' Response: We would be reluctant to go much deeper into DHR in this paper, as it has been extensively described in other papers. As such we feel that a detailed description of the method in this paper would unnecessarily lengthen what is already a long manuscript and would not add to the already extensive literature on DHR. A sentence has been added within the methods section to lead readers to the best papers providing more detail on DHR should they wish to read further on the subject: "The method is described in detail by Taylor et al. (2007), Young (1998) and Young et al. (1999) and as such only a brief outline of the technique is provided below". A paragraph has also been added to the conclusions to highlight why DHR proved a valuable tool in analysing the NO3 time-series.

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R2 Comment 2: The time series analysis of the dataset is a very important contribution given the lack of this kind of analysis in river and stream work (seems like most is in oceanography and climate fields). Any additional detail that you see as relevant to moving the water quality studies in this direction (and challenges, particularly related to sample density and auto-correlation) would be appreciated.

Authors' Response: The authors agree that time series analysis has a key role to play in interpreting the complex dynamics being revealed through the collection of high frequency hydrochemical data. However, we feel that in this paper the remarks made in the conclusions about the future direction of catchment monitoring are sufficient for the moment. An exploration of how time series techniques could be used to move water quality studies forward would be a paper in its own right.

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R2 Comment 3: Given that you have a figure on DON (Fig.3), it seems like you should at least include more info in the methods on lab analysis.

Authors' Response: We have updated the methods section to include this. Fig. 3 has now been removed and replaced with a figure showing the explanatory variables.

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R2 Comment 4: Your section on the "significance of diurnal cycling" is important - while an interesting process that will yield insights into ecosystem dynamics, I applaud you for putting it in a broader context of watershed N cycling and retention.

Authors' Response: We thank Dr Pellerin for his comment on this section. We agree that it is vital to put the diurnal instream NO3 dynamics within the context of catchment scale N cycling.

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R2 Technical Comments: The paper is very well written and only a few technical details need to be addressed –

P. 13144: Please clarify what "1983/1990" means?

Authors' Response: Addressed - Text now reads "Non-significant increasing trends were observed in inorganic N concentrations in the rainfall and cloud water between the start of the records in 1983 and 1990, respectively, and 1997"

Section 5.4 title: needs space

Authors Response: Addressed

Interactive comment on Biogeosciences Discuss., 10, 13129, 2013.

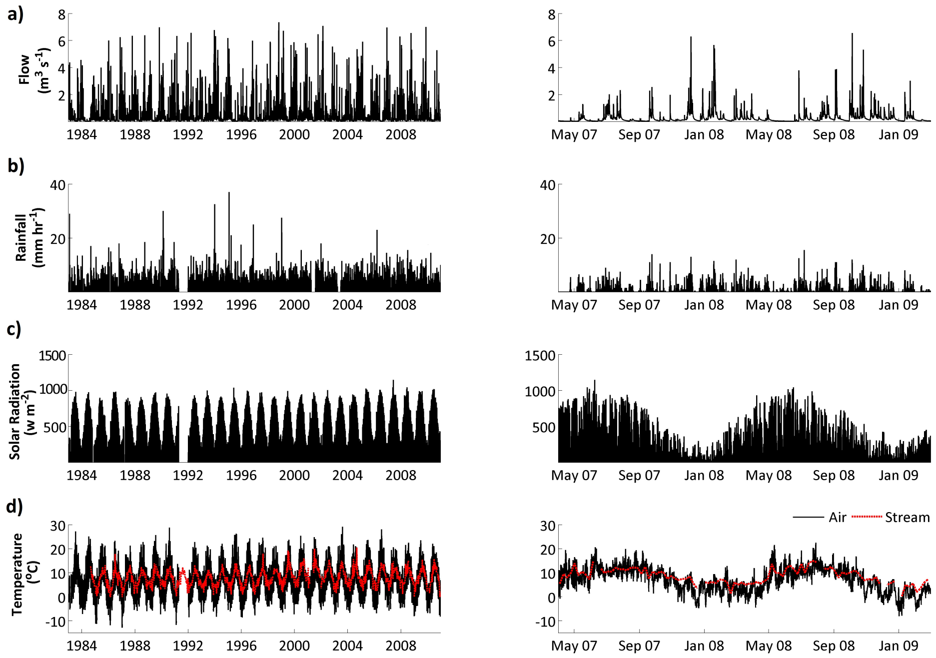

Fig. 1. Explanatory variables (New Figure 6)