

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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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.

C5023

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. 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.

Controls on Diurnal Nitrate Variation: Second, considerable time is spent evaluating the controls on diurnal nitrate variation, and particularly the lag behind 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 so-

C5024

lar 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 production 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).

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).

Inferences about Diurnal Variation: Finally, I had two minor comments on inferences

C5025

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. 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.

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.

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C5026