Landscape heterogeneity drives contrasting concentration-discharge relationships in shale headwater catchments

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Final Response

Anonymous Referee #1
Review of hessd-12-2013-2015
Title: Biotic controls on solute distribution and transport in headwater catchments, by Herndon et al.

General comments

The manuscript concerns concentration-discharge relationships in two contrasting sites in terms of landscape distribution of soil organic matter and connectivity to the stream, including a total of three headwater catchments. This is an interesting and relevant topic as there is a need to shed light on the role of different and heterogeneous landscape configurations on catchment biogeochemical processes. It is argue that elements closely related to biotic cycling or involved in organic complexes (distributed more heterogeneously over the catchment) show no chemostatic behavior, whereas those elements more connected to weathering processes are chemostatic with respect to discharge. These results should be of interest to the scientific community in general and the HESS readers in particular.

Overall, the paper is well-structured and written and easy to follow, but I have several minor and major concerns about its present form, especially regarding the focus that the authors give to the role of vegetation. I would recommend addressing all questions, comments, and suggestions listed below before this manuscript can be accepted for publication in HESS.

One of the main ideas that the paper wants to transmit is that vegetation is the major driver of solute transport. This is supported by the comparison of two sites with the same underlain material but different organic matter pattern. But the sites also differ in terms of climate and hydromorphology, which I would suggest are the central players. The paper would benefit if the focus given to the role of vegetation is lowered. Certainly, not all the solutes presented have a biological origin or are influenced by vegetation cycling besides the interaction with organic matter. It is not convincing that the fact that certain solutes are associated with organic matter is sufficient reason to define them as "bioactive". Many metals, some of which are presented in this paper, are organophilic and therefore have affinity to bind and be transported together with organic matter. Largely, this is controlled by hydrogeochemical processes that do not necessarily involve biological activity to a large extend; therefore I would argue define these elements as "bioactive" is misleading.

We have removed the word "bioactive" from the text given that there is not clear delineation between bioactive and organophilic solutes. We now focus on the influence of landscape heterogeneity rather than vegetation on concentration-discharge relationships. For example, the title has been changed to "Landscape heterogeneity drives contrasting concentration-discharge relationships in shale headwater catchments." We do not have sufficient evidence to determine how climate and hydromorphology drive the landscape distribution of SOM in these catchments;

however, we discuss factors that generally lead to heterogeneous distribution of SOM across landscapes. For example:

l. 334-343. In the following sections, we discuss how the landscape distribution of chemically distinct pools and the connectivity between organic-rich soils and the stream control how concentrations vary with discharge. We contend that the behavior of certain elements are non-chemostatic in these systems due to their association with organic matter. The distribution of soil organic matter across landscapes is in turn influenced by climate (e.g., SOM generally increases with increasing moisture and decreasing temperatures on large geographic scales) and geomorphology (e.g., organic matter accumulates in depressed areas such as swales on small geographic scales).

It is not clear how the solute concentrations in the pore water and groundwater are related to stream water as there was no connectivity assessment presented from the places were the soil water was taken. It can be argue that these might not be representative of the stream water, especially when there is heterogeneity within the soils. I acknowledge the use of ratios but it would be interesting to show or present more clearly what is the hydrological connection between the soils sampled and the stream.

At Shale Hills, our conceptual model for hydrological connectivity is based on patterns of soil moisture and hillslope transport reported for the catchment. We sampled pore waters from soils on planar and swale hillslopes and evaluated their connection to the stream based on the reported connection of planar and hillslope soils to the stream.

We have expanded the description of hydrological connection in the methods to provide a framework for understanding solute transport:

l.137-140. Soils in swales are generally wetter than soils on planar hillslopes and remain hydrologically connected to the stream during dry periods, whereas water flow through planar hillslopes is negligible under dry conditions and increases with increasing precipitation (Lin et al., 2006; Qu and Duffy, 2007).

The following assessment of hydrologic connectivity at Shale Hills is also presented in the discussion:

l.350-355. At Shale Hills, meteoric water passes through the thin organic horizon and organic-rich A horizon (< 15 cm deep) and is transported along the horizon interfaces to the stream via preferential flow paths (Lin et al. 2006; Jin et al., 2011; Thomas et al., 2013). The stream receives water from organic-rich swales and surface soils during dry periods, and water inputs from organic-poor hillslope soils increase as the catchment saturates (Qu and Duffy, 2007; Andrews et al. 2011).

l.360-362: Stream chemistry did not reflect inputs from groundwater during dry periods, consistent with a previous finding that the water table drops to > 2 m below the stream bed during late summer (Thomas et al., 2013).

At Plynlimon, pore water chemistry was not available for soils within the catchments; therefore, we used available data reported for these soil types sampled throughout Plynlimon. The hydrological connection of the forested and peat soils to the stream are based on previous literature, e.g. l.174:

l.170-178: Generally, the main flow paths in both catchments are approximately orthogonal to the valley direction, with highly fractured shallow bedrock providing an important pathway and storage for water throughout the catchments, especially under base flow conditions (Haria and

Shand, 2004; Shand et al., 2005(a-b); Shand et al., 2007). Shallow and deeper groundwater appear to be poorly connected but some mixing does occur (Haria and Shand, 2004; Shand et al., 2005b; Shand et al., 2007). Flow in organic horizons, however, tends to be largely lateral rather than vertical, providing minimal water-rock interaction in peat dominated portions of the catchment and increasing contribution to streams during high flow conditions (Shand et al., 2009).

The paper also presents some interesting results in relation to harvesting, but as it is presented now it appears as a residual part of the study. This should be either expanded or omitted. I would suggest expanding it. For example, there is no mention to this topic on the introduction. It could be also expanded in the discussion with comparisons to other studies, and presented in the conclusions.

The comparison of pre-harvest and post-harvest C-Q relationships in the Upper Hore has been expanded. Specifically, we now plot the post-harvest C-Q data in Figure 2 (see end of response) and include tree harvest results in the abstract (l. 42-45), introduction (l. 109-110), discussion (l. 393-412), and conclusions (l. 497-499).

The catchments in Plynlimon are notably bigger than the catchment in Shale Hills. How can this have influenced the results in terms of comparison?

We did not explicitly investigate the role of catchment area on concentration-discharge patterns, and it is not expected that catchment size will influence the observed concentration-discharge patterns. For example, Godsey et al. (2009) found that catchment area was not a significant factor influencing concentration-discharge relationships of major weathering elements (Ca, Mg, Na, Si) in a long-term analysis of 59 diverse catchments. Catchment size may be more important in event-based studies where changes in stream chemistry are monitored over time-scales on which the lag-time in stream flow and groundwater level response to precipitation become important (e.g., McGlynn et al., 2004).

Throughout the paper, there is a lack of emphasis on when in time the data are from.

We have included more detailed information on sampling times in the methods (l. 143-145; l. 159-162; l. 189-191), tables (2-4), and Figure 2.

There are several citations in the text that are missing in the reference list. I note most of them below in the technical corrections. The present study is built up from previous work, accordingly cited, but it feels that the paper lacks some other relevant literature for the topic. This is especially important in the discussion, where more literature is needed to support and compare the findings of this work and to put the results in context.

The reference list has been updated to include all citations in the text. We have included additional citation throughout the introduction and discussion sections to put our results in context of prior and ongoing work, particularly with regard to studies on CQ behavior, vegetation influences on stream chemistry, and watershed models.

Specific comments

Title

I would suggest reformulate the title so the term "biotic" is not included. It can be misleading as the paper does not present specifically any biological experiments or large biological data.

As discussed above, the title has been changed to "Landscape heterogeneity drives contrasting concentration-discharge relationships in shale headwater catchments".

Abstract

P. 214; L. 3-5: Please, reformulate so it is clear that it is three headwater catchments you are comparing, which are located in two different sites. It would also be interesting for the reader to know the catchments sizes at this point.

We have amended the text as follows: "In a comparison of three shale-underlain headwater catchments located at two sites in Pennsylvania, USA (Shale Hills) and Wales, U.K. (Plynlimon)…"

The information on catchment size has been omitted from the abstract for the sake of brevity but is provided in the methods (l. 124 and l. 165-168).

1. Introductions

P.215; L.18: The terms "groundwater" and "pore water" need to be defined and differentiated at some point as they are used throughout the paper. Is the term groundwater referring to the soil water permanently below the water table and pore water referring to that water intermittently below the water table? Does the pore water concept here also include water that is never below the water table?

In l.88-89 of the introduction, we have added the following:

Throughout this paper, groundwater is defined as water that is stored in catchment soils and bedrock below the water table, and pore water is defined as water that is present in the pores of unsaturated soil in the vadose zone.

P.215; L.23: Unclear what is meant by "These trends". Bishop et al. (2004) approach has been applied for different solutes and in different catchments; the problem of their approach is the use of individual transects (maybe not representative of the entire catchment) to explain stream water chemistry. Thus, the relevance of the present paper is to emphasize the need to account for heterogeneity within a catchment.

We have amended this sentence to better reflect current literature on CQ trends (l.76-79):

Although changing flow paths through soil horizons may explain differences in solute response to discharge along hillslope transects (e.g., Bishop et al., 2004), solutes often show different types of behavior in different streams due to landscape heterogeneity, and a unifying explanation for C-Q behavior has remained elusive.

P. 216; L. 2-5: But the water that comes from upslope still needs to pass through the riparian zone before reaching the stream and the chemical signal can change (as it is actually explained in L. 5-10). Please, reformulate so this point is made clearer.

We have amended the sentence as follows to discuss the origin of the water, rather than the flow itself, during changing flow regimes:

Stream chemistry can vary during storm events as dominant water inputs to the stream shift from groundwater and riparian zones during base flow to hillslope runoff at high flow as pore waters stored in upland soils become increasingly connected to the stream (McGlynn and McDonnell, 2003a).

P. 216; L. 13-14: "Many previous studies examine catchments that were developed on multiple lithologies," Could you cite some examples?

We have amended the sentence to include "single catchments and/or catchments developed on multiple lithologies" and have included a number of pertinent references (e.g., Johnson et al., 1969; Krám et al., 1997; Brown et al., 1999; Likens and Buso, 2006; Godsey et al., 2009).

P. 216; L. 17: Could you add "three" in front of "shale-underlain. . ."

"Three" has been added to l. 104.

P. 216; L. 18-20: Is it possible that the differences in distribution of vegetation and SOM are caused by climatic and hydromorphological factors (which seem to be different in the two sites)? Then, should not this be the main drivers of the differences between the two sites?

We address the influence of climate and hydromorphology on SOM distribution in the discussion (l.332-339) and have changed this sentence to more specifically outline the differences in SOM between the catchments:

l. 104-108: Although these catchments are underlain by chemically similar shales, their soils have developed distinct and contrasting distributions of SOM across each landscape; i.e., organic-rich soils are predominantly in low-lands and swales in the Shale Hills Critical Zone Observatory but in upland peat regions of the Upper Hore and Upper Hafren catchments in the Plynlimon forest.

2. Methods

P. 217; L. 22-23: Could it be implied from this that the local hydromorphology is what controls the generation and mobilization of DOC, and therefore many other carbonrelated compounds? I believe so.

See discussion above.

P. 218; L. 1: What is the uncertainty of discharge measurements?

No uncertainty estimates have been provided with the dataset (Duffy, 2012) or in a publication that utilizes the dataset (Thomas et al., 2013), but the measurements are stated to be very accurate.

P. 218; L. 3-6: What is the distance to the stream of the soil water and groundwater measurements?

As shown in Figure 1, the soil water and groundwater were sampled within 10 m of the stream.

P. 218; L. 4: How many lysimeters? Until what depth?

Additional details on lysimeters have been added as follows (l. 150-153):

Soil water was collected from suction lysimeters installed in the soil at 10 cm depth increments from 10 to 50 cm depth in the south planar valley floor (SPVF) and from 10 to 90 cm depth in the south swale valley floor (SSVF).

P. 219; L. 1: What is the uncertainty of discharge measurements?

Uncertainty in measured discharge at Plynlimon is reported to be low (~2.5% over the period of study [Marc and Robinson, 2007, Hydrol. Earth Syst. Sci. 11(1), 44-60]).

P. 219; L. 7: What wells in Fig. 1? The distribution of wells in relation to the stream and the time when they were sampled (also in relation to the stream) is unclear.

This sentence has been changed to indicate that we analyzed groundwater chemistry from all wells shown in Figure 1:

l. 187-190: Groundwater chemistry was estimated as average concentrations of solutes in seven shallow (< 3 m) wells located within the Plynlimon forest near the two catchments (Figure 1). Wells were sampled weekly from 1994 – 1999 (Neal et al., 1997) (Table A1).

P. 219; L. 9: What is the temporal and spatial variation in pore water chemistry within the different classes? Is it sufficiently low that the use of average values is justified? Maybe, the data presented in table 3 should be introduced here to support this. In that case, table 2 should be also presented before, in section 2.1.

Spatial and temporal variability in pore water chemistry were not evaluated because we focused on differences amongst soil types; given our focus, we present averages and standard errors calculated from all available data for each soil type. Standard error measurements are used to differentiate pore water chemistry amongst soil types. The following sentence has been amended to clarify this and to reference Table 3:

l. 190: Average solute concentrations (± standard error) were calculated for pore waters sampled from soils classified as peat, stagnopodzol, or peaty gley throughout Plynlimon (Reynolds et al., 1987; Reynolds et al., 1988; Stevens et al., 1997; Shand et al., 2005) (Table 3; Table A2).

Similarly, a reference for Table 2 has been added to section 2.1.

3. Results

P. 220; L. 3: According to Table 4, the slope for Mg at Upper Hore is lower than the previously set limit for chemostatic behaviour at -0.1. Therefore this should be expressed as "Na and Mg behaved near-chemostatically. . ."?

The text in line 219 has been changed to "near-chemostatically" to reflect the m_{Mg} values of -0.11 and -0.12 in the Upper Hore.

P. 220; L. 3: In Table 4, the Upper Hore catchment results are divided into per- and post-harvest whereas in Figure 2 are presented together. Why?

The data from the Upper Hore presented in Figure 2 included only pre-harvest data, while the post-harvest data were included in Figure A6. To clarify that the data were evaluated separately, as presented in Table 4, the post-harvest data have been moved from the supporting information to Figure 2 (panels i-k).

P. 220; L. 6-9: It seems that there is a lack of statistical significance (Figure 2; Table 4) in most of the slopes of the solutes defined as "bioactive". For example, it is not so obvious that DOC decreased with

discharge at Shale Hills (clearer in Fig S2), or that Mn and K increased at Plynlimon. This point should be outlined better.

As indicated in footnote b in Table 4, all slopes were significant to p < 0.001 except where explicitly stated. We have included the following sentence in section 2.3 to clarify our statistical methods:

l. 211: Linear regressions and associated statistical parameters were calculated in Origin 8 (OriginLab).

P. 220; L. 14: Please, indicate which time period this refers to.

In l.236, we have indicated that the "dry summer season" refers to June through September.

P. 220; L. 24: Could you remind here which solutes exhibited enrichment?

The sentence has been changed to "In contrast, solutes exhibiting enrichment (K, Al, Mn, Fe, DOC) varied by season (Figures A3 and A4)."

P. 220; L. 25-28: Belongs to discussion.

This sentence has been moved to the discussion (l. 383-386).

P. 221; L. 10-11: An assessment of what is the connectivity to stream of the places where pore water was sampled has not been presented or proved. It can be argue that these might not be representative of the stream water, especially when there is heterogeneity within the soils.

Please see comment above for further discussion of hydrological connectivity.

P. 222; L. 10-11: Belongs to discussion.

This sentence has been removed from the results and integrated with a similar sentence in the discussion as follows:

l. 317-320: No significant correlation (p > 0.05) existed between organic to mineral pore water ratios and m_j in the Upper Hore and Upper Hafren subcatchments, likely because organic horizons at Plynlimon have high concentrations of chemostatic solutes due large inputs of sea salts that dominate the chemical signature of near-surface pore waters.

P. 222; L. 13-24: This feels like it could be moved to the methods section or at least introduced partially there (potentially as a 2.4 section).

The methods for the mixing diagrams have been moved to section 2.3 and the results have been integrated with section 3.2

P. 223; L. 16: Please, could you change "behaviour" by "relationship"?

In l.302, "concentration-discharge behaviors" has been changed to "concentration-discharge relationships", although we note that behavior is commonly used in the literature.

4. Discussion

P. 224; L. 25-26: I would argue that is the landscape configuration (i.e. hydromorphology), together with climate, what drives vegetation and vegetation patterns.

See above discussion regarding controls on SOM distribution.

P. 225; L. 2: Please, reconsider the use of the term "bioactive" throughout the paper.

The term bioactive has been removed throughout the paper; rather, we use the term "non-chemostatic" to discuss the behavior of elements formerly designated bioactive.

P. 226; L. 1: Is vegetation really accumulating all the so-called "bioactive" elements during drier growing season? From the data presented is not possible to infer this. In any case it seems that the regulation is made by the climate, and thereby soil moisture and hydrologic connectivity rather than by vegetation itself.

We contend that it is important to distinguish between climate and vegetation when discussing the C-Q relationships of these elements. If hydrological connectivity was the only factor influencing C-Q, we may expect that all elements behave similarly. Rather, SOM accumulation and biological activity (i.e., uptake by vegetation) create spatially and temporally distinct chemical pools within catchments. Although climate ultimately drives SOM distribution and biological activity, SOM and vegetation impact the C-Q relationships of certain elements more than others. We interpret that the C-Q relationships for these non-chemostatic elements in the Upper Hafren are regulated by vegetation based on long-standing literature that documents seasonal variability in stream concentrations of nutrient elements due to biological uptake (e.g., Johnson et al., 1969; Vitousek, 1977; Mulholland, 1992).

l. 5. Conclusions

P. 229; L. 17-19: This is the main message of the paper and I believe important but it is not necessarily the vegetation what is controlling the concentration-discharge relationships. Hydrologic connectivity is an important factor that is highlighted here and could be highlighted more in other parts of the paper instead of vegetation.

Please see comment above for further discussion. Our discussion of hydrological connectivity of soils to the stream has been expanded; however, we contend that vegetation and SOM are an additional important factor that create the chemically distinct pools.

References

Please, expand your literature to support your results and put them in context.

We have included more citations and discussion of previous research, particularly with regard to the role of vegetation in regulating stream chemistry.

Figures and Tables

Table 2: Please, indicate the periods of time in which these averages are based on.

Time periods of collection have been added for each site and sample type.

Table 3: Please, indicate the periods of time in which these averages are based on.

Time periods of collection have been added for each site and sample type.

Figure 2: Please, add the periods of time in which the relationships are based on. Could all panels have the same scale in the axes?

Time periods have been added for the Upper Hore to distinguish pre-harvest and post-harvest data. The time periods of collection for the Upper Hafren and Shale Hills catchments are given in Tables 2-3 and in the text.

Axes are the same scales in all panels with the exception of the x-axes in the panels for Shale Hills (a, b). The range of discharge at Shale Hills is lower than the range in the Plynlimon catchments, and the authors use different scales to allow the data to be best visualized by the reader.

Figure 4: Please, show R2 for (b) and (c) too (in the caption).

R^2 values have been added to the Figure 4 caption as follows:

Specifically, m_j was (a) negatively correlated with the ratio of solute concentrations in organic-rich versus organic-poor soil waters at Shale Hills ($R^2 = 0.90$, $p < 0.001$) and positively correlated with the ratio of solute concentrations in pore waters versus precipitation in (b) the Upper Hafren ($R^2 = 0.48$; $p < 0.05$) and (c) the Upper Hore ($R^2 = 0.42$; $p < 0.05$).

Technical corrections

1. Introduction

P.215; L.2: Please, use either watershed or catchment throughout the paper.

       The text has been changed to specifically refer to these sites as catchments.

P.215; L.10: Maher (2011) is missing in the reference list. **- corrected**

P.215; L.16: Clow and Mast (2010) is missing in the reference list. **- corrected**

P.215; L. 27-28: These two citations are missing in the reference list. **- corrected**

P. 216; L. 2: Pringle (2001) is missing in the reference list. **- corrected**

P. 216; L. 12: Köhler et al. (2014) is missing in the reference list. **- corrected**

2. Methods

P. 217; L. 23: Andrews et al. (2011) is missing in the reference list. **- corrected**

3. Results

P. 220; L. 3: Table 4? Table 2 and 3 have not been presented yet. Should the tables be presented in order? That is, this could be renamed as table 2.

Citations for Tables 2 and 3 are now included in the methods section and all tables are presented in order.

P. 220; L. 23-24: Neal and Kirchner (2000) is missing in the reference list. **- corrected**

P. 222; L. 16: Gaillardet et al. (1999) is missing in the reference list. **- corrected**

P. 223; L. 9: Please, change "A7" by "S7".

The figure is labeled A7 in accordance with HESS formatting.

P. 224; L. 1: Qu and Duffy (2007) is missing in the reference list. **- corrected**

4. Discussion

P. 225; L. 22: Thomas et al. (2013) is missing in the reference list. **- corrected**

P. 228; L. 6: Evangelou and Phillips (2005) is missing in the reference list. **- corrected**

References

Please, include all the missing references. **- corrected**

Anonymous Referee #2

The paper "Biotic controls on solute distribution and transport in headwater catchment" by Herndon et al fits well to the HESSD journal context. Its strength is in multi-disciplinarily as the paper is written on the borderline between hydrology and soil chemistry. In this review I assume that the main audience for the paper is from the field of hydrology. From this respect I would rather see it as a skillful attempt to learn more about the flow pathways and runoff contributing areas for 3 catchments with similar lithology but different topographical settings and placed in different climate and vegetation zones. It uses the established empirical (and unique for each catchment) relationships between the soil pore water source and chemistry in vertically and horizontally heterogeneous landscape (mixing model). The study also shows that SOM distribution within the catchment, its placement and connectivity to streams has a strong predictive power for DOC and other solutes. The approach is quite novel and deserve publication and the only major comment I have to the presentation of hydrology is that the catchments have been well studied before, as authors says, e.g. with an isotopes technique. So I would advise to extent the comparison between the authors' conclusions about the flow path with what previously have been found using other techniques.

Based on recommendations from all reviewers, we have included more text detailing hydrological connectivity of soils to the stream for each site (see response above to Reviewer #1). Information on hydrological connectivity derived from previous studies is now included in the methods section (site information), discussion, and Figure 1.

The authors also pursued another purpose – to develop key conceptual component for predictive model of solute transport in headwater catchment. If that has to be evaluated I feel little confidence in my own expertise and would rather advice to send the paper for an additional reviewer whose major would be in pure soil chemistry. I could advice Ed Tipping's group at the Centre for Ecology & Hydrology in Lancaster Environment Centre, but certainly there many others. My concern here is that the key for understanding of why particular solute behaves differently in different geographical settings has to be based on detailed analysis of the cation binding and dissociation by humic and fulvic acids. Few aspects can be critical: 1) Cation exchange sites are saturated with different exchangeable cations in podzol and peat soils 2) The degree of saturation by exchangeable cations differs between the studied soils and is indeed a factor of vegetation and soil water regime (P-E). It also varies largely vertically being maximum in illuvial horizons. 3) The ability of mineral soil particles to adsorb organic molecules depends on the solution Fe, Al, Ca and Mg concentration. On the other side complexes can be formed between the fulvic acids and metals. So it is not straight forward to see causality (DOC vs. metals). 4) The lateral transport trough inhomogeneous soil is will modify the chemistry that simple source mixing model would propose

We acknowledge that these factors are important for regulating solute concentrations in pore waters and thus transport into streams; however, it is beyond the scope of this paper to provide a detailed reaction-transport model for these sites. We intend for this study to provide a platform for investigating such processes (e.g., through reactive transport models) that will provide a mechanistic basis for the empirical trends highlighted here.

In p. 228 authors provide the cation exchange capacity for different soils, but the statement "degree of chemostatis was inversely related to the elements' relative strength of adsorption to cation exchange sites" seems critical for the process understanding, and yet no figure or table support it. I would also think it is fruitful to follow this consideration while explaining why one element is chemostatic in one setting and is not in another.

The comparison here is necessarily qualitative because we do not have quantitative data for the strength of cation adsorption to exchange sites. We have also amended the sentence to indicate that

the degree of chemostasis is influenced by cation exchange for <u>chemostatic elements</u>; whether an element is chemostatic or non-chemostatic at different sites is likely driven by the landscape heterogeneity, as described in the rest of the manuscript.

Minor comments:

I would advice writing the solutes with a charge because they all are ions, e.g. Ca2+ not just Ca

We cannot definitively state the charge or speciation for all elements and, for uniformity, request to represent them as elements rather than ions. For example, Fe may be present as the solutes Fe(2+) or Fe(3+) or in colloids that pass through a 0.45 µm filter.

Abstract: L7. I would suggest "by patterns of vegetation and SOM" I would also explain already here that there are 2 catchments within Plynlimon catchment: one is peatland (heath) dominated and another is forest dominated

The suggested revisions have been made as follows:

In a comparison of three shale-underlain headwater catchments located in Pennsylvania, USA (the forested Shale Hills Critical Zone Observatory) and Wales, U.K. (the peatland-dominated Upper Hafren and forest-dominated Upper Hore in the Plynlimon forest), dissimilar concentration-discharge behaviors are best explained by contrasting landscape distributions of soil solution chemistry – especially dissolved organic carbon (DOC) – that have been established by patterns of vegetation and soil organic matter.

P.217 Please provide a soil type for the Shale Hills watershed.

The following information has been added (l. 125-128):

Shale Hills contains primarily Inceptisol soils developed from shale residdum or colluvium of the Rose Hill Formation, which is dominantly comprised of clay minerals and quartz (Lin et al., 2006; Jin et al., 2010). Small areas of Ultisols are present near the stream (Lin et al., 2006).

P.228 L.14 "on mineral surfaces'. Also on fulvic and humic acids surfaces and organomineral complexes.

The sentence has been amended to clarify the role of organic matter in the exchangeable pool (l. 457-459):

Thus, chemostasis is explained by increasing connectivity of the exchangeable pool, i.e., cations bound to surfaces of minerals and soil organic matter, to mobile water as soil saturation increases.

Comment by A. Wlostowski

The objective of this paper is to elucidate the controls on concentration discharge relationships by comparing to catchments with similar underlying lithologies, however different distributions of SOM, and different climatic settings. The key take home message, in my opinion, is that concentration discharge relationships are highly dependent on the nature of hydrological connections within any given catchment. Nonchemostatic elements were found to be distributed more heterogeneously within catchments, as opposed to more chemostatic elements. Overall, I strongly believe that this paper contributes to an ongoing discussion of understanding hydrologic controls on geochemical processes in watersheds throughout the world, and is worthy of eventual publication. However, I have a few suggestions for improving this manuscript:
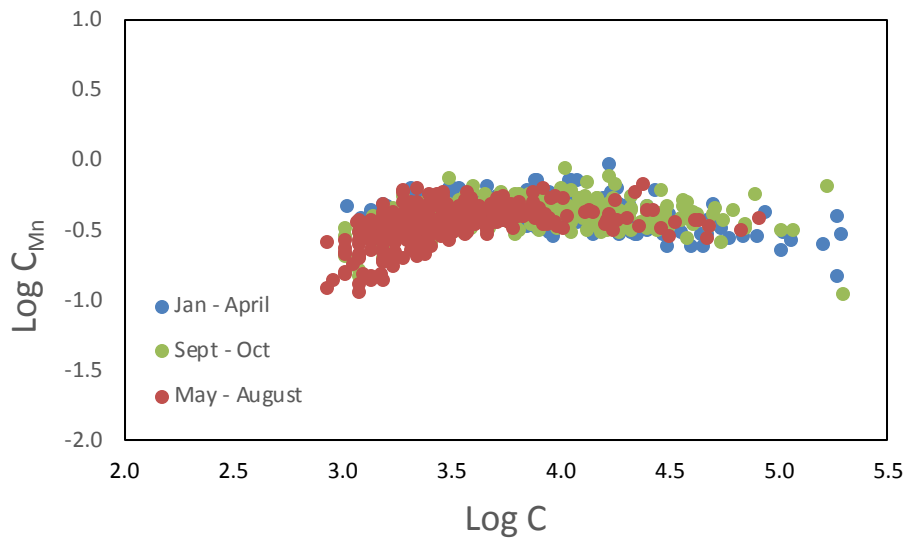
1 - The authors discuss the seasonal variations in element concentrations, discharge patterns, and precipitation regimes. These seasonal variations are then used to support seasonally dependent conceptual models (for example, page 226, section 4.1, lines 4-8). However, the C-Q regression analyses were all completed by using all the data, taking a single regression to explain all times of the year and flow conditions. I wonder what we can learn by sub sapling this data set to look at C-Q relationships during drier v. wetter periods. This analysis could be done by using time as a threshold between the dry and wet seasons, or by using simple discharge thresholds to define dry v. wet catchment states. When I look at the data shown in Figure 2, some of the relationships are not completely linear. For example, Figure 2f, it seems like Na and Mg show more of a dilution signal above $logQ = 4.5$. Or, Figure 2g, Mn is enriched at a greater rate when $logQ$ is less than 3.7. I encourage the authors to interrogate these slope breaks a bit further. Perhaps the rationale would relate back to the degree of hydrologic connectivity in the catchment under drier versus wetter conditions?

The C-Q relationships were evaluated with simple linear regressions fit to all the data in order to facilitate comparison amongst elements and between catchments. In the case of Shale Hills, the dataset is sparse, and the relationships become less significant with subsampling. However, we do note that not all C-Q relationships are strictly linear, and the non-linearity may reflect transitions in hydrological connectivity, such as the transition from swale to hillslope soils at Shale Hills. Through subsampling the datasets, we find that a few slopes vary by season but mostly because the subsampled datasets occupy different regions of the overall C-Q trend (but are overlapping) indicating that is the non-linearity is driven by flow regime rather than season. We have included discussion of elements with pronounced non-linearity (examples as follows) but do not include discussion of more subtle variations in slope given that we cannot adequately quantify relative contributions of different waters that may lead to these signals.

l. 356-358: Increasingly negative slopes for non-chemostatic elements at high discharge (Figure 2b) may reflect the transition in hydrologic connectivity and hillslope inputs to the stream.

l. 386-388: At high flow, decreases in Mn concentrations in the stream (Figures 2d and 2g) may reflect the low abundance of Mn in the catchment relative to other elements; in other words, the supply of Mn is depleted at high flow and Mn is diluted in the stream.

For reference, we provide a log-log plot of C vs Q for Mn at Plynlimon to demonstrate that the trend is driven by discharge rather than season (i.e., the trend is consistent regardless of season).

Log C_{Mn}

1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0

● Jan - April
● Sept - Oct
● May - August

2.0   2.5   3.0   3.5   4.0   4.5   5.0   5.5

Log C

2 - The big idea of this paper would be greatly improved by a conceptual model cartoon. Can you generate a final figure for section 4.1 of this paper that illustrates how the hydrochemical connections differ between shale hills and Plynlimon? The idea is discussed very well with text, but having a visual would improve the overall understanding of this idea.

In addition to providing more background on hydrologic connectivity at each site, we've modified the caption for Figure 1 to highlight how hydrologic connectivity interacts with landscape heterogeneity at each site. The landscape features shown in Figure 1 best demonstrate our conceptual model: organic-rich soils are in the lowlands at SH and uplands at Plynlimon, leading to differences in water chemistry as water flows through those soils in different quantities. For Shale Hills, existing models of hydrologic connectivity have been previously published (Lin et al., 2006; Qu and Duffy, 2007)

Figure 1 caption edits: Brown and green shading delineate major landscape features that are organic-rich or organic-poor in each catchment: swale versus planar slopes at Shale Hills or peat versus forested regions at Plynlimon. Notably, the most organic-rich soils are in lowlands in Shale Hills but uplands in Plynlimon; consequently, inputs from organic-rich soils dominate stream flow under low-flow conditions in Shale Hills but high-flow conditions in Plynlimon.

3 - Can you make any arguments or suggestions as to how watershed modelers might improve model selection or parameterization to better account for hydrochemical interactions? You acknowledge this as a problem in on page 215, section 1, lines 5-7. In my opinion, this paper argues for more spatially explicit watershed models (perhaps TOPMODEL?) which can simulate the wetting up and drying down of individual hill slopes within a catchment. A large portion of the HESS audience is watershed modelers, so including some discussion of modeling lessons we might learn from this study would be nice.

We have included the following discussion in section 4.1 to highlight how current models can be improved to consider factors such as landscape heterogeneity:

Previous studies have hypothesized that hydrologic connectivity within landscapes (McGlynn and McDonnell, 2003a; Hood et al. 2006; Clow and Mast 2010) and/or interactions between soil moisture and mineral reactive surface area (Godsey et al. 2009; Clow and Mast 2010) can explain concentration-discharge relationships across multiple catchments. Our results contribute to the understanding of solute behavior by highlighting the importance of hydrologic connectivity across landscapes and at mineral surfaces. At both Shale Hills and Plynlimon, the distribution of soil organic matter and its hydrologic connection to the stream governed non-chemostatic concentration discharge behavior of several solutes (Ca, K, Mn, Fe and Al), a process similarly invoked to explain stream DOC behavior in storm events (McGlynn and McDonnell, 2003b). Our results highlight the need to include or enhance reactive transport modules (RTM) in spatially-distributed watershed-scale hydrologic models such as TOPMODEL (Beven and Kirkby 1979), the Penn State Integrated Hydrologic Model (PIHM; Qu and Duffy 2007), and the Regional Hydro-Ecological Simulation System (RHESSys; Band et al. 1991). Specifically, combining RTM with the ability of spatially-distributed models to simulate soil moisture, temperature, and water fluxes at variable depths across geomorphic features (e.g., swales vs. planar slopes) will allow researchers to elucidate specific flow water paths and transit times and better test drivers of chemostasis (cation exchange) and dynamics of mobile vs. immobile water. RT-Flux-PIHM is one model under development (Duffy et al. 2014) that will provide this platform, but it is imperative to cross-compare outputs from various models in order to reach consensus.

Updated Figure 2:
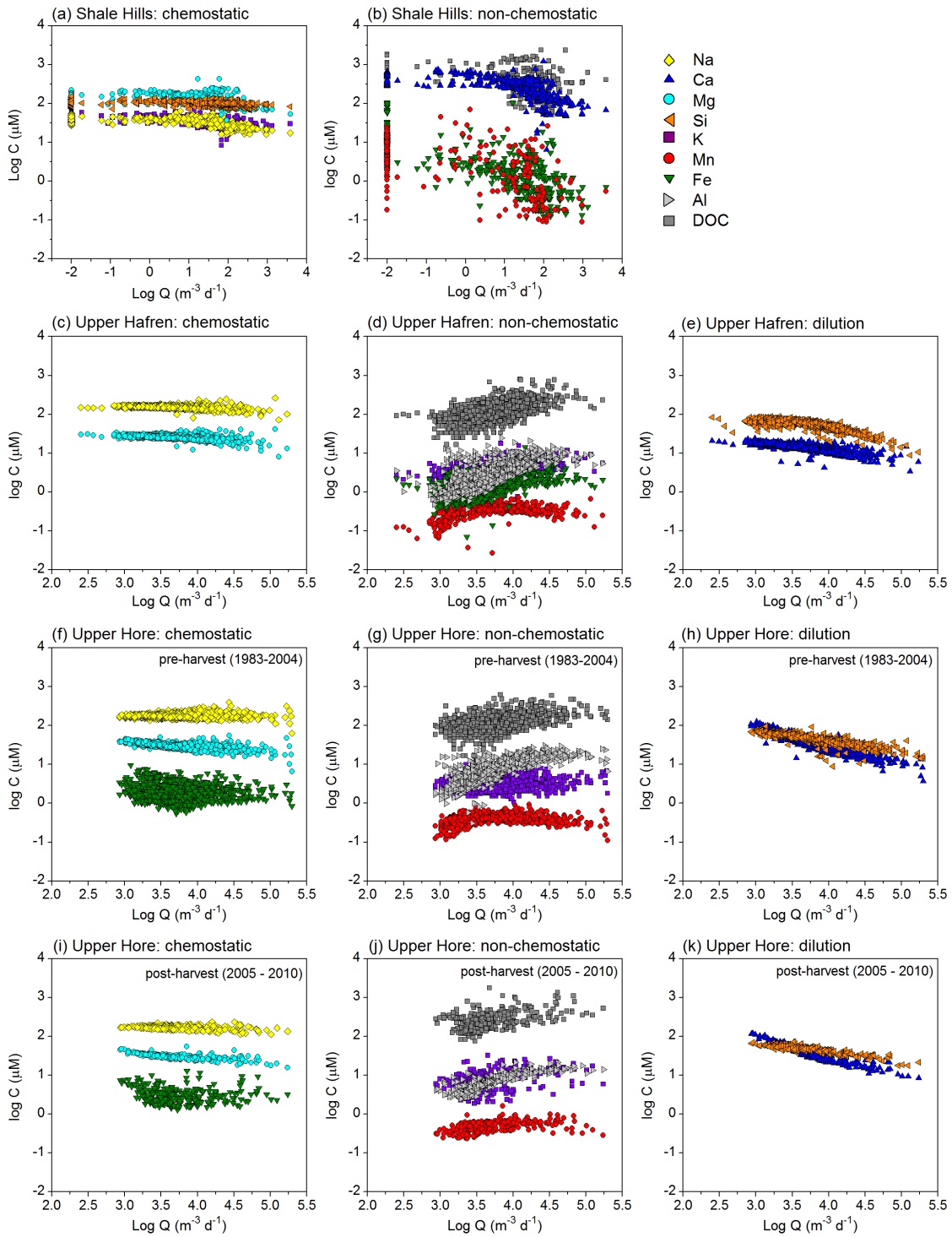
~~Biotic c~~Landscape heterogeneity drives~~ontrols~~ ~~on solute distribution and transport~~ contrasting concentration-discharge relationships in shale headwater catchments

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Abstract

Solute concentrations in stream water vary with discharge in patterns that record complex feedbacks between hydrologic and biogeochemical processes. In a comparison of three shale-underlain headwater catchments ~~underlain by shale in~~located in Pennsylvania, USA (the forested Shale Hills Critical Zone Observatory) and Wales, U.K. (the peatland-dominated Upper Hafren and forest-dominated Upper Hore in the Plynlimon forest), dissimilar concentration-discharge behaviors are best explained by contrasting landscape distributions of soil solution chemistry – especially dissolved organic carbon (DOC) – that have been established by patterns of vegetation and soil organic matter (SOM). Specifically, elements that are concentrated in organic-rich soils due to biotic cycling (Mn, Ca, K) or that form strong complexes with DOC (Fe, Al) are spatially heterogeneous in pore waters because organic matter is heterogeneously distributed across the catchments. These solutes exhibit non-chemostatic ~~"bioactive"~~ behavior in the streams, and solute concentrations either decrease (Shale Hills) or increase (Plynlimon) with increasing discharge. In contrast, solutes that are concentrated in soil minerals and form only weak complexes with DOC (Na, Mg, Si) are spatially homogeneous in pore waters across each catchment. These solutes are chemostatic in that their stream concentrations vary little with stream discharge, likely because these solutes are released quickly from exchange sites in the soils during rainfall events. Furthermore, concentration-discharge relationships of non-chemostatic solutes changed following tree harvest in the Upper Hore catchment in Plynlimon, while no changes were observed for chemostatic solutes, underscoring the role of vegetation in regulating the concentrations of certain elements in the stream. These results indicate that~~D~~differences in the hydrologic connectivity of organic-rich soils to the stream drive differences in concentration behavior between catchments. As such, in catchments ~~where soil organic matter (SOM~~SOM~~)~~ is dominantly in lowlands (e.g. Shale Hills), we infer that ~~bioactive~~ non-chemostatic elements associated with organic matter are released to the stream early during rainfall events, whereas in catchments where SOM is dominantly in uplands (e.g. Plynlimon), ~~bioactive~~ these non-chemostatic elements are released later during rainfall events. The distribution of ~~vegetation and~~ SOM across the landscape is thus a key component for predictive models of solute transport in headwater catchments.

Keywords

1 Introduction

Streams are regularly monitored to evaluate watershed geochemistry, ecosystem health, and suitability for human use. However, streams integrate hydrologic and biogeochemical processes over varied spatial and temporal scales, making it difficult to determine both the sources and flow paths of solutes. While many researchers examine short- to long-term element variability in stream water, it has remained difficult to derive generalized models quantifying solute concentration-discharge behavior (Fisher et al. 2004; Sivapalan 2005; Zimmer et al. 2012). Flow paths may dictate stream chemistry by controlling fluid residence times and chemical equilibration of flowing water with soil minerals within catchments (Maher, 2011). Therefore, it is necessary to understand how heterogeneous flow paths through distinct chemical sources within a catchment influence observed solute concentration patterns within streams.

When the discharge of a stream (Q) increases, concentrations of solutes (C) can either increase (enrichment behavior), decrease (dilution behavior), or, perhaps most paradoxically, change very little (chemostasis) (Kirchner, 2003; Godsey et al., 2009; Clow and Mast, 2010). Dilution can result during rainfall events as water stored in a catchment is diluted by less concentrated meteoric water. Enrichment can result if a more concentrated source (e.g. groundwater) mixes with stream water during large rainfall events (Johnson et al. 1969). In contrast, chemostasis cannot be explained by the simple mixing of multiple sources and therefore has been attributed to processes such as chemical reactions with the solid-phase along the pathway of water flow (Godsey et al. 2009). ~~These trends can be~~Although changing flow paths through soil horizons may explain differences in solute response to discharge along hillslope transects ~~explained for an individual solute or single catchment~~ (e.g., Bishop et al., 2004), ~~but~~ solutes often show different types of behavior in different ~~catchments~~streams due to landscape heterogeneity, and a unifying explanation for C-Q behavior has remained elusive.

Behavior differences amongst individual solutes in the stream have been linked to variability in solute concentrations within a catchment: in other words, discrete zones of element mobilization within soils and sediments can lead to pulses of solute transport into a stream (McClain et al., 2003; Andrews et al., 2011). This effect is furthermore affected by changes in hydrologic connectivity, defined as the water-mediated transfer of constituents between water sources (Pringle, 2001), within a catchment during rainfall events. Stream chemistry can vary during storm events as ~~flow~~ dominant water inputs to the stream shift~~s~~ from groundwater and

riparian zones during base flow to ~~upslope soil pore waters~~hillslope runoff at high flow as pore waters stored in upland~~s~~ soils become increasingly connected to the stream (McGlynn and McDonnell, 2003a). Throughout this paper, groundwater is defined as water that is stored in catchment soils and bedrock below the water table, and pore water is defined as water that is present in the pores of unsaturated soil in the vadose zone. ~~Such connectivity of upland soils can occur if~~Upland soils become hydrologically connected to the stream when soil layers become water-saturated, promoting downslope flow within the unsaturated zone. As a result, concentrations of solutes that are stored preferentially in the riparian zone, e.g. dissolved organic carbon (DOC) released from soil organic matter (SOM), peak in the stream prior to discharge or with rising discharge during storm events (McGlynn and McDonnell, 2003b; Hood et al. 2006). Variability in organic carbon dynamics across different landscape units can subsequently control metal export from headwater catchments and downstream hydrochemistry (Köhler et al., 2014).

Many previous studies examine single catchments and/or catchments that were developed on multiple lithologies (e.g., Johnson et al., 1969; Krám et al., 1997; Brown et al., 1999; Likens and Buso, 2006; Godsey et al., 2009)~~,~~, making the interpretation of solute behaviors difficult at best. When mono-lithologic catchments are compared, insights into other factors that influence the response of stream chemistry to discharge~~C-Q behavior~~ (e.g. biota, climatic) can be developed. To elucidate controls on stream chemistry not primarily driven by lithology, we examined C-Q ~~behaviors~~ relationships in three shale-underlain headwater streams with extensive hydrogeochemical datasets. Although these ~~watersheds~~ catchments are underlain by chemically similar shales, their soils have developed distinct and contrasting distributions of ~~vegetation and~~ SOM across each landscape; i.e., organic-rich soils are predominantly in low-lands and swales in the Shale Hills Critical Zone Observatory but in upland peat regions of the Upper Hore and Upper Hafren catchments in the Plynlimon forest. Additionally, we investigate how C-Q patterns change following tree harvest in the forested Upper Hore. For these ~~watersheds~~catchments, variations in stream chemistry with flow elucidate non-lithological factors that control solute transport to streams, yielding a paradigm that should help explain other catchments.

2 Methods

Water chemistry was compared for three sites: 1) the Susquehanna Shale Hills Critical Zone Observatory (Shale Hills) in central Pennsylvania, USA and 2) the Upper Hore and 3) Upper

Hafren subcatchments in the Plynlimon experimental forest in Wales, UK (Figure 1). The Shale Hills and Plynlimon forests are underlain almost exclusively by Fe-rich, organic-poor, Silurian-aged shale formations that are stratigraphically equivalent. Although these headwater catchments vary by size and location, their similar lithologies and extensive hydrogeochemical characterization (e.g. Kirby et al., 1991; Neal et al., 1997; Shand et al., 2006; Jin et al., 2010; Neal et al., 2011; Brantley et al., 2013(a-j); Dere et al., 2013) allow development of a unifying theory on factors controlling concentration-discharge behavior.

2.1 Susquehanna Shale Hills Critical Zone Observatory

Shale Hills is an 8 ha forested headwater catchment nested within the larger Susquehanna River Basin in Pennsylvania, USA. Shale Hills ~~is underlain~~contains primarily inceptisol soils developed from shale residuum or colluvium of the ~~by the~~ Rose Hill Formation, which ~~contains~~ is dominantly comprised of clay minerals and quartz (Lin et al., 2006; Jin et al., 2010). Small areas of ultisols are present near the stream (Lin et al., 2006). The regional mean annual temperature (MAT) is 10°C, and precipitation (MAP = 105 ± 17 cm y^{-1}) is acidic (e.g., pH averaged 4.5 ± 0.2 for U.S. National Atmospheric Deposition Program (NADP) sites PA15 & PA42 during 2000-2011). Vegetation is dominated by deciduous oaks and hickories, and the elevation ranges from 256 m at the catchment outlet to 310 m on the ridge. Hillslopes are characterized as either "planar" (mildly convex-upward slopes with shallow soils that grade to concave-upward slopes toward valley floor) or "swale" (concave-upward depressions with deep soils and convergent water flow) (Lin et al., 2006) (Figure 1). Water flows vertically through pores when soils are unsaturated, or downslope along horizon interfaces when rainfall events create transiently perched saturated water zones (Lin, 2006; Jin et al., 2011). Soils in swales are generally wetter than soils on planar hillslopes and remain hydrologically connected to the stream during dry periods, whereas water flow through planar hillslopes is negligible under dry conditions and increases with increasing precipitation (Lin et al., 2006; Qu and Duffy, 2007; Takagi and Lin, 2012). Soils in the swales also store more organic carbon than soils on planar hillslopes and act as sources of DOC transport into streams (Andrews et al., 2011) (Table 1).

Water samples from Shale Hills were collected approximately daily from the stream outlet (2008 – 2010) and biweekly from soil lysimeters (2006 – 2011) from March through early December each year~~2006-2011~~ (Table 2). Detailed methods and results of chemical analyses,

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including isotopic variation and concentrations of major ions and DOC, have been reported elsewhere (Jin et al., 2011; Andrews et al., 2011; Brantley et al., 2013(a-j)). Aluminum concentrations in the stream were consistently below detection limits; thus, Al data were not examined for Shale Hills. Average dDaily discharge rates were estimated from continuous discharge measurements collected atintegrated over 10 min intervals from the stream weir at the catchment's outlet (Duffy, 2012). Soil water was collected from suction lysimeters installed in the soil at 10 cm depth increments from 10 to 50 cm depth in the south planar valley floor (SPVF) and from 10 to 90 cm depth in the south swale valley floor (SSVF) soils. The groundwater was sampled from a 2.8 m deep well located 80 m upstream from the weir. Major cation (2000-2011; NADP, 2011) and trace element concentrations (Herndon, 2012) have been reported for precipitation samples collected from NADP sites PA-15 and PA-42. Vegetation chemistry was previously determined for green leaf and leaf litter samples collected throughout summer and fall seasons, respectively, in the Shale Hills catchment (Herndon et al., 2015).

2.2   Plynlimon forest: Upper Hore and Upper Hafren catchments

The Plynlimon forest is a 682 ha watershed located at the headwater of the River Severn, 20 km from the west coast of Wales (Reynolds et al., 1997). MAT is 7.2 °C and MAP is 250 ± 78 cm with an average pH of 4.98 ± 0.01. Vegetation is predominantly evergreen Sitka spruce (*Picea sitchensis*) with areas of heath, including *Sphagnum* and *Juncus* communities, dominating the uplands. Elevation in the Plynlimon forest ranges from 319 to 738 m.

We focus on two adjacent headwater catchments within the Plynlimon watershed: the Upper Hore and the Upper Hafren (Figure 1). The Upper Hore (162 ha) is predominantly forested with periodically saturated, organic-rich stagnopodzol soils and uplands that are dominated by grass and saturated peat soils (Kirby et al., 1991). In contrast, the Upper Hafren (122 ha) is dominated by heath and peat soils, with waterlogged and organic-rich peaty gley soils located in riparian areas (Kirby et al., 1991). Generally, the main flow paths in both catchments are approximately orthogonal to the valley direction, with highly fractured shallow bedrock providing an important pathway and storage for water throughout the catchments, especially under base flow conditions (Haria and Shand, 2004; Shand et al., 2005(a-b); Shand et al., 2007). Shallow and deeper groundwater appear to be poorly connected but some mixing does occur (Haria and Shand, 2004; Shand et al., 2005b; Shand et al., 2007). Flow in organic horizons, however, tends to be largely

lateral rather than vertical, providing minimal water-rock interaction in peat dominated portions of the catchment and increasing contribution to streams during high flow conditions (Shand et al., 2009).

Stream chemistry data for the Upper Hore and Upper Hafren catchments were collected throughout the year for all years between 1983-2005 and 1990-2010, respectively (Neal et al., 2013a and 2013b). Due to extensive tree-cutting in the Upper Hore in 2005, data collected from 2005-2010 were evaluated separately to examine the influence of tree removal on C-Q behavior. Stream discharge was measured every 15 min at weirs in both catchments and weekly stream grab samples were analyzed for major and trace ions. Likewise, bulk precipitation was collected weekly at the Carreg Wen meteorological station located between the Upper Hore and Upper Hafren catchments (Reynolds et al., 1997). Precipitation chemistry was influenced by seawater inputs, which varied with wind direction and season (Reynolds et al., 1987). Groundwater chemistry was estimated as average concentrations of solutes in seven shallow (< 3 m) wells located near the weirs within the Plynlimon forest near the two catchments (Figure 1). Wells were sampled weekly from 1994 – 1999 (Neal et al., 1997) (Figure 1; Table A1). Average pore water chemistry was calculated for all Average solute concentrations (± standard error) were calculated for pore waters sampled from sampled soils classified as peat, stagnopodzol, or peaty gley throughout Plynlimon (Reynolds et al., 1987; Reynolds et al., 1988; Stevens et al., 1997; Shand et al., 2005) (Table 3; Table A2).

2.3 Stream flow regimes and concentration-discharge (C-Q) behaviors

To analyze discharge events To analyze stream chemistry under different flow regimes, stream water discharge (Q, m^3 d^{-1}) was categorized as low-flow (lower quartile of Q), moderate-flow (interquartile range), or high-flow (upper quartile) (Figure A1). Perennial stream flow with little seasonal variation in discharge was observed in the Upper Hafren and Upper Hore catchments, and the distributions of Q were positively skewed by intermittent storms. Stream flow at Shale Hills was intermittent and highly seasonal, with extended periods of no- to low-flow during summer months (especially July and August). Solute concentrations for each flow regime at each site were averaged over all collection dates (Tables 2 and 3).

Linear regressions were fit to log-transformed C-Q data for each solute j (C_j) for each catchment stream. We included all available data for all years for Shale Hills (2008 – 2010), the

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The slope of this regression (m_j) was used to identify solute behaviors as "chemostatic" or "non-chemostatic". When m_j showed only minimal effects of dilution by meteoric water, i.e., $-0.1 < m_j < 0$, the solutes were defined as chemostatic (Godsey et al., 2009). In contrast, non-chemostatic elements were defined to exhibit dilution behavior when concentrations decreased with increasing Q ($m_j < -0.1$) or enrichment behavior when concentrations increased with increasing Q ($m_j > 0$). Linear regressions and associated statistical parameters were calculated in Origin.

To investigate sources of solutes mobilized to the stream, element ratios in the stream under different flow regimes were compared to element ratios in pore waters, precipitation, groundwater, and leaves (where available). Element ratios have been used in other studies to link river chemistry to end member reservoirs (e.g. Gaillardet et al., 1999). Molar ratios of divalent cations (Ca:Mg) were compared to univalent cations (K:Na) in each reservoir to understand how elements exhibiting non-chemostasis (Ca, K) vary relative to chemostatic elements (Mg, Na). To further explore the association of certain non-chemostatic solutes with organic C, molar ratios of Mn (a non-chemostatic element) to Mg were compared to DOC concentrations. Average DOC concentrations were used to define soil waters as organic-rich or organic-poor, as discussed in section 3.2. In Shale Hills, green leaves were used to represent the most organic-rich end-member since pore waters could not be sampled from the thin O horizon.

3 RESULTS

3.1 Solute concentration-discharge patterns

Na and Mg behaved near-chemostatically in all catchments (Figure 2; Table 4) while Si and K were only chemostatic at Shale Hills. A subset of non-chemostatic solutes exhibited similar trends to DOC; however, trends were opposite between Shale Hills and Plynlimon. Specifically, when Q increased, concentrations of the non-chemostatic solutes Ca, Mn, Fe and DOC decreased at Shale Hills (i.e. dilution behavior; $m_j < -0.1$) while the non-chemostatic solutes Mn, K, Al, Fe, and DOC increased at Plynlimon (i.e. enrichment behavior; $m_j > 0$) (Figure 2b; Table 4). Note that Fe exhibited enrichment ($m_{Fe} = 0.33 \pm 0.02$) similar to DOC in the Upper Hafren but

was more consistent with chemostasis in the Upper Hore (m_{Fe} = -0.05 ± 0.02). Additionally, Si and Ca showed dilution patterns at Plynlimon that contrasted with DOC.

In the Shale Hills stream, higher concentrations of stream solutes were observed during the dry summer season (June through September) relative to the wetter spring and autumn (Figure A2). While concentrations of the chemostatic elements increased only slightly (~2X) during the summer, larger increases were observed for Ca (~4X), DOC (~7X), and Mn and Fe (> 100X). Increases in DOC, K, Fe, and Mn in the stream during summer were not consistent with increasing groundwater inputs because groundwater at Shale Hills is depleted in these elements relative to stream water at low flow (Table 2). In the Upper Hafren and Upper Hore streams, chemostatic elements Na and Mg, derived primarily from sea salts, showed no seasonality despite high seasonal variation in inputs from precipitation (Figure A5; Reynolds et al., 1987), as if precipitation-derived solutes were buffered in the catchment soil pore waters before entering the stream (Neal and Kirchner, 2000). In contrast, solutes exhibiting enrichment (K, Al, Mn, Fe, DOC) varied by season (Figures A3 and A4). Although groundwater can discharge to streams in Plynlimon during summer months (Shand et al., 2005), the groundwater contains little DOC (Table 3) and therefore cannot explain changes in summer stream chemistry where DOC increases from spring to summer (Figures A3 and A4).

In the Upper Hore where trees were harvested, solute concentrations and C-Q slopes increased following tree harvest for solutes showing enrichment behavior. Specifically, stream concentrations of DOC, K, Mn, and Fe increased after 2005 (Table 3). Post-harvest values ofC-Q slopes for m_K (= 0.26 ± 0.03) and m_{Mn} (= 0.12 ± 0.02) increased relative to pre-harvest values (0.07 ± 0.01 and 0.05 ± 0.01, respectively) (Figure 2 A6; Table 4). No effects of tree harvest on C_j or m_j were observed for chemostatic elements. Additionally, no changes in solute concentrations in the non-harvested Upper Hafren were observed over this time.

3.2   Soil pore waters

We examined the chemical composition of soil pore waters in order to investigate sources of solutes to the stream. Pore waters in each catchment were categorized into distinct chemical pools based on DOC concentrations (Table 2): "organic-rich" waters were defined by average DOC > 1 mM, while all other waters were "organic-poor". At Shale Hills, pore waters collected from the A horizon (10 cm) of the swale (SSVF) were organic-rich (1.28 ± 0.33 mM DOC)

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while all other pore waters were organic-poor; i.e. the A horizon of SPVF (0.69 ± 0.06 mM DOC) and the B horizons of SSVF and SPVF (> 10 cm; averaged 0.55 ± 0.04 mM DOC) were organic-poor. At Plynlimon, pore waters in organic horizons and peat soils (1.2 ± 0.2 mM DOC) were organic-rich relative to mineral horizons of stagnopodzol and peaty gley soils (0.42 ± 0.07 mM DOC) soils.

At Shale Hills, concentrations of the non-chemostatic solutes Mn, Fe, and Ca showed evidence of DOC-related behavior. For example, Mn and Fe were positively correlated with DOC across all pore waters ($R^2 > 0.9$) and were highest in the organic-rich waters (6.8 ± 1.9 μM and 1.7 ± 0.3 μM, respectively) (Table 2). Calcium concentrations were enriched in the A horizon (72 ± 11 μM) relative to the B horizon (35 ± 1 μM) in SSVF. Furthermore, Fe and Mn concentrations were spatially variable across pore waters (% RSD = 100% and 140%, respectively). In contrast, chemostatic solutes Mg (33%), Na (19%), and Si (5%) were less variable. Thus, concentrations of non-chemostatic solutes were spatially heterogeneous in soil waters across the landscape while chemostatic solutes were distributed more homogeneously.

Like Shale Hills, concentrations of the chemostatic elements Na and Mg were spatially homogeneous in pore waters at Plynlimon amongst the different soils (RSD = 23% and 15%, respectively) (Table 3). Additional solutes chiefly derived from the atmosphere via precipitation (K, Ca) or through carbon fixation (DOC) were enriched in the organic horizons, while elements derived primarily from minerals (Si, Fe, Al, and Mn) were enriched in mineral horizons. In contrast to Shale Hills, many of the non-chemostatic elements at Plynlimon were not correlated with DOC in soil pore waters. This is likely due to the fact that organic horizons at Plynlimon receive large inputs of sea salts that dominate the chemical signature of near-surface pore waters.

3.3 Mixing diagrams

To investigate sources of solutes that are mobilized to the stream, element ratios in pore waters, precipitation, groundwater, and leaves (where available) were compared to element ratios in the stream. Element ratios have been used in other studies to link river chemistry to end member reservoirs (e.g. Gaillardet et al., 1999). Molar ratios of divalent cations (Ca:Mg) were compared to univalent cations (K:Na) in each reservoir to understand how elements exhibiting non-chemostasis (Ca, K) vary relative to chemostatic elements (Mg, Na). To further explore the association of certain non-chemostatic solutes with organic C, molar ratios of Mn (a non-

chemostatic element) to Mg were compared to DOC concentrations. Average DOC concentrations were used to define soil waters as organic-rich or organic-poor, as discussed in section 3.2. In Shale Hills, green leaves were used to represent the most organic-rich end-member since pore waters could not be sampled from the thin O horizon.

Element ratios in stream water under low, moderate, and high flow regimes were compared to element ratios in pore waters, precipitation, and groundwater (Figure 3). At Shale Hills, stream chemistry was most similar to pore waters from organic-rich soils and green leaves at low flow and approached values for pore waters from organic-poor soils at high flow. Ratios of $C_{Ca}:C_{Mg}$ and $C_K:C_{Na}$ decreased slightly (< 2X) with increasing discharge (Figure 3a), while $C_{Mn}:C_{Mg}$ decreased by 10X (Figure 3b). Stream water was more similar to soil pore waters than groundwater or precipitation under all flow regimes, documenting that flow through shallow soils and bedrock rather than deep groundwater sources dominated inputs to the stream. These trends further indicate a shift from inputs of organic-rich soil water to the stream at low flow to organic-poor soil water at high flow.

In contrast to this behavior at Shale Hills, stream chemistries in the Upper Hore and Upper Hafren catchments were most similar to organic-poor sources (precipitation, groundwater) at low flow and organic-rich sources (soil pore waters) at high flow (Figure 3c-f; Figure A7). Values of $C_{Mn}:C_{Mg}$, C_{DOC}, and $C_K:C_{Na}$ increased while $C_{Ca}:C_{Mg}$ decreased and converged towards the most organic-rich end-member in each system, either the peat (Upper Hafren) or peat and organic horizon pore waters (Upper Hore), with increasing discharge. Stream $C_{Ca}:C_{Mg}$ ratios were similar to groundwater at low flow in the Upper Hafren. The limited groundwater data that were available for Plynlimon indicate that groundwater was not chemically similar to stream water under any flow regime in the Upper Hore (Figure 1).

3.43   Organic influence on concentration-discharge behavior

Finally, we explored how chemical heterogeneity in soil pore waters influenced concentration-discharge behaviors relationships in the streams. Specifically, we evaluated solute heterogeneity due to redistribution by vegetation as the ratio of solute concentrations in "organic-rich" to "organic-poor" pore waters. As previously defined, these pore waters were collected from A versus B horizons at Shale Hills, and organic versus mineral soils in the Upper Hafren and Upper Hore. The slope of the concentration-discharge plot (m_j) was used to define the

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magnitude of non-chemostatic behavior for each solute, i.e. the degree to which an element was diluted or enriched in the stream with increasing discharge.

At Shale Hills, elements concentrated in the organic-rich pore waters were diluted rapidly in the stream with increasing discharge, consistent with increasing inputs of water from mineral soils as the planar hillslope soils become saturated during storms (Qu and Duffy, 2007). This trend is documented in Figure 4a where the concentration ratios for organic-rich versus -poor soil waters were negatively correlated with respect to m_j ($R^2 = 0.90$, $p < 0.001$). According to these results, Fe and Mn were most concentrated in organic-rich pore waters and most rapidly diluted in the stream, followed by DOC, Ca, and K. Chemostatic elements Na, Mg, and Si were not concentrated in organic-rich pore waters.

No significant correlation ($p > 0.05$) existed between organic to mineral pore water ratios and m_j in the Upper Hore and Upper Hafren subcatchments, likely because organic horizons at Plynlimon have high concentrations of chemostatic solutes due ~~to atmospheric inputs.~~ large inputs of sea salts that dominate the chemical signature of near-surface pore waters. Provided this observation, organic-associations in each catchment were evaluated by inspecting the ratio of average solute concentrations in the pore water versus precipitation (Figure 4b,c), i.e., precipitation serves as the most organic-poor pool in the Plynlimon system. For both the Upper Hafren and the Upper Hore, the ratios of concentrations in soil water versus precipitation were positively correlated with m_j ($p < 0.05$). Elements exhibiting enrichment behavior, including DOC, Al, Mn, and K in both catchments plus Fe in the Upper Hafren, were also enriched in pore water relative to precipitation. Chemostatic elements in pore waters were less enriched relative to precipitation. In contrast, the ratios for soil water versus precipitation were not significantly correlated with m_j at Shale Hills ($p > 0.05$).

4 Discussion

Cross-site comparison of the Shale Hills and Plynlimon headwater catchments revealed that the behaviors of non-chemostatic solutes were controlled by the spatial variability of those elements in soil waters and the distribution of DOC. Conversely, chemostatic solutes were homogeneously distributed in pore waters across the catchments. In the following sections, we discuss how ~~vegetation drives~~ the landscape distribution of chemically distinct pools~~;~~ ~~subsequently,~~ and the connectivity between organic-rich soils and the stream control~~s~~ how

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concentrations vary with discharge. We contend that the behavior of certain elements are non-chemostatic solutes in these systems should be defined as "bioactive" due to their association with organic matter. The distribution of soil organic matter across landscapes is in turn influenced by climate (e.g., SOM generally increases with increasing moisture and decreasing temperatures on large geographic scales) and geomorphology (e.g., organic matter accumulates in depressed areas such as swales on small geographic scales).

4.1   Hydrologic connectivity of solute pools across landscapes

At first glance, it may appear contradictory that bioactive element concentrations of non-chemostatic elements in the streams at Shale Hills and Plynlimon trend in opposite directions with increasing discharge; however, the discrepancy can be explained by differences in the distributions of organic-rich source waters in each system. Similar to bioactive elements identified by Stallard and Murphy (2013), we attribute the non-chemostatic concentration-discharge behavior of bioactive solutes to changing water flow through organic-rich soil matrices; however, we also observe that organic-rich sources and flow paths vary between the catchments (Figure 1).

At Shale Hills, meteoric water passes through the thin organic horizon and organic-rich A horizon (< 15 cm deep) and is transported along the horizon interfaces to the stream via preferential flow paths (Lin et al. 2006; Jin et al., 2011; Thomas et al., 2013). The stream receives water from organic-rich swales and surface soils during dry periods, and water inputs from organic-poor hillslope soils increase as the catchment saturates (Qu and Duffy, 2007; Andrews et al. 2011). Consequently, we observed that stream water chemistry was similar to organic-rich soil waters at low flow and organic-poor soil waters at high flow (Figure 3). Solutes derived largely from organic-rich soils exhibited greater variability over different flow regimes due to their high spatial variability in soil pore water. Increasingly negative slopes for non-chemostatic elements at high discharge (Figure 2b) may reflect the transition in hydrologic connectivity and hillslope inputs to the stream. Stream chemistry did not reflect inputs from groundwater during dry periods, consistent with a previous finding that the water table drops to > 2 m below the stream bed during late summer (Thomas et al., 2013).

In the grass-dominated Upper Hafren, which contains peat soils that experience minimal water-rock interaction (Kirby et al., 1991), concentrations of chemostatic elements in the soils

never deviate~~d~~ far from an average precipitation signal (Figure 4). In contrast, concentrations of ~~bioactive~~non-chemostatic elements ~~we~~are not driven by precipitation, and we propose that pore water concentrations of these elements are ~~attributed to regulation~~regulated by vegetation. ~~D~~During the drier growing season, ~~bioactive~~certain non-chemostatic elements ~~are~~may be depleted from soil pore water and accumulate~~d~~ in vegetation, leading to lower concentrations in the stream. Indeed, it is well-established that seasonal uptake by vegetation regulates concentrations of nutrient elements in stream water (e.g., Johnson et al., 1969; Vitousek, 1977; ~~.~~ Mulholland, 1992). ~~Drying of the surface peat and higher temperatures~~Warming and drying of the surface peat during this time increase~~s~~ microbial decomposition, thereby increasing mobility of ~~bioactive~~ elements that accumulate in vegetation by releasing them from storage in organic matter (Kirby et al., 1991). According to this conceptual model, once transpiration decreases and flow increases through the soil in autumn, concentrations of ~~bioactive~~these elements increase in the stream because 1) transpiration is reduced and the soil water is no longer being depleted; 2) the surface peat is flushed of elements that have accumulated, providing elements in addition to precipitation. As observed at the Upper Hafren and Upper Hore, concentrations of ~~bioactive~~non-chemostatic elements begin to increase in the stream as discharge increases following low-flow in the summer (Figures A3 and A4). This effect may be especially prominent in the peat regions since the grass vegetation decomposes annually with little aboveground storage (i.e. peat is leaky with respect to nutrients), and anoxic conditions limit complete conversion of SOM to CO_2, enhancing release of DOC. Although groundwater can discharge to streams in Plynlimon during summer months (Shand et al., 2005), the groundwater contains little DOC (Table 3) and therefore cannot explain changes in summer stream chemistry where DOC increases from spring to summer (Figures A3 and A4). At high flow, decreases in Mn concentrations in the stream (Figures 2d and 2g) may reflect the low abundance of Mn in the catchment relative to other elements; in other words, the supply of Mn is depleted at high flow and Mn is diluted in the stream.

In the spruce-forested Upper Hore, long-term storage of nutrient elements in above-ground biomass is expected to deplete soil pore waters of ~~bioactive~~ elements without the flushing effect due to rapid turnover observed in the Upper Hafren (Reynolds et al., 2000). Instead, the positive concentration-discharge slopes in the Upper Hore result from flushing of upland peat soils at high flow conditions (Neal et al., 1990). These effects can be observed by comparing pre- and

post-harvest concentration-discharge slopes in the Upper Hore. Tree harvest impacted stream concentrations and C-Q slopes for K, Al, Fe, Mn, and DOC but had no observable effects on chemostatic elements. Specifically, m_K increased from 0.07 to 0.25 following harvest, while the peat-dominated Upper Hafren, which was not harvested, maintained $m_K = 0.15$ during this time. Fe and DOC experienced increases in stream concentrations, but not m_j. Since neither Fe nor DOC is expected to be taken up into the trees in high quantities, increasing C_j may indicate that they were mobilized by increased decomposition of leaf litter debris in the forest region following harvest (Hughes et al., 1990).

Values of C_j and m_j values for bioactivenon-chemostatic, organic-associated elements likely increased following harvest because 1) these elements were no longer being taken up and stored in tree biomass (Stevens et al., 1997); 2) the organic debris left after harvest provided a labile pool of organic chelator molecules and bioactiveorganically-complexed elements, and 3) inputs from upland peats to the stream increased due to lack of interception by the forest (Neal et al., 1992; Neal et al., 2004). Such short-term increases in nutrient loss following ecosystem disturbance are well documented, especially for clear-cut systems (e.g., Likens et al., 1970; Vitousek, 1977; Neal et al., 1992). Although bioactivenon-chemostatic in the Upper Hafren, Fe followed a chemostatic trend in the Upper Hore (Figure 2). This behavior could be due to Fe retention in the forested soils during downslope transport: stagnopodzols on these slopes have Bs horizons that accumulate sesquioxides and immobilize leached Fe (Reynolds, 1982).

Previous studies have hypothesized that hydrologic connectivity within landscapes (McGlynn and McDonnell, 2003a; Hood et al. 2006; Clow and Mast 2010) and/or interactions between soil moisture and mineral reactive surface area (Godsey et al. 2009; Clow and Mast 2010) can explain concentration-discharge relationships across multiple catchments. Our results contribute to the understanding of solute behavior by highlighting the importance of hydrologic connectivity across landscapes and at mineral surfaces. At both Shale Hills and Plynlimon, the distribution of soil organic matter and its hydrologic connection to the stream governed non-chemostatic concentration discharge behavior of several solutes (Ca, K, Mn, Fe and Al), a process similarly invoked to explain stream DOC behavior in storm events (McGlynn and McDonnell, 2003b). Our results highlight the need to include or enhance reactive transport modules (RTM) in spatially-distributed watershed-scale hydrologic models such as TOPMODEL (Beven and Kirkby 1979), the Penn State Integrated Hydrologic Model (PIHM; Qu and Duffy

2007), and the Regional Hydro-Ecological Simulation System (RHESSys; Brand et al. 1991). Specifically, combining RTM with the ability of spatially-distributed models to simulate soil moisture, temperature, and water fluxes at variable depths across geomorphic features (e.g., swales vs. planar slopes) will allow researchers to elucidate specific flow water paths and transit times and better test drivers of chemostasis (cation exchange) and dynamics of mobile vs. immobile water. RT-Flux-PIHM is one model under development (Duffy et al. 2014) that will provide this platform, but it is imperative to cross-compare outputs from various models in order to reach consensus.

4.2   Drivers of chemostasis

Stream concentrations for most major weathering elements (j = Na, K, Mg, Ca, Si) varied little over a wide range of discharge values (Figure 2): by this definition, most of the major elements were chemostatic, with the exception of Ca at Shale Hills and K at Plynlimon. Note that the standard descriptor "major elements" includes Na and Ca although both are low in abundance in the protolith at Shale Hills and Plynlimon (< 0.7 wt.% and < 0.2 wt.%, respectively), ~~while~~ and K is lower at Plynlimon compared to Shale Hills (2.90 wt.% and 3.76 wt.%, respectively) (Jin et al., 2010; Dere et al., 2013). Chemostasis could be expected for elements derived from minerals that are always equilibrated with long residence-time pore waters. However, the fast-dissolving minerals present at Shale Hills and Plynlimon, carbonates and pyrite, do not contain K, Na and Si and are also depleted in the upper protolith (Jin et al., 2010; Neal et al., 1997). Therefore, dissolution of these minerals cannot explain chemostasis of K, Na, Si, Mg and Ca. Godsey et al. (2009) suggested that changes in mineral-water interfacial area during periods of high and low discharge explain chemostasis; however, clay dissolution rates are too slow (Bandstra et al., 2008) to provide a rapidly mobilized source of cations during the short-timescales of precipitation events.

The exchangeable cation pool is a likely source of chemostatic elements during rain events (e.g., Clow and Mast, 2010). The cation exchange capacity of soils along the planar hillslope at Shale Hills ranges from 35 to 71 meq kg^{-1} (Jin et al., 2010). At Plynlimon, forest and peat soils have a cation exchange capacity of roughly 77.4 and 300 meq kg^{-1}, respectively (Reynolds et al., 1988; Cuttle, 1983). Elements are displaced from cation exchange sites into solution by H^{+} (i.e. protonation of the exchange sites), and we observe that the degree of chemostasis for

~~chemostatic elements~~ was inversely related to the elements' relative strengths of adsorption to cation exchange sites ~~as reported by~~ (Evangelou ~~and Phillip~~set al~~.~~-. (2005). Furthermore, this explanation can even account for the highly chemostatic, neutrally charged solute $Si(OH)_4^0$, which has also been documented in the exchangeable pool at Shale Hills (Jin et al., 2010). For these catchments where pH is low (pH < 7), Si should be weakly associated to exchange sites due to its neutral charge. The similar concentrations observed for major weathering elements in the planar and swale pore waters at Shale Hills as well as Plynlimon (Tables 2 and 3) are attributed to the quick exchange of protons in rain for cations in the exchange pool throughout the catchment. Thus, chemostasis is explained by increasing connectivity of ~~the exchangeable cation pool on mineral surfaces~~ the exchangeable pool, i.e., cations bound to surfaces of minerals and soil organic matter, to mobile water as soil saturation increases.

4.3 Chemostatic ~~elements~~ nutrients become ~~bioactive~~non-chemostatic under ~~nutrient~~ nutrient-limiting conditions

Although geochemically similar to Mg, K, and Na, the concentration-discharge pattern for Ca (Figure 2) ~~suggests it exhibits a degree of bioactive behavior~~is non-chemostatic at Shale Hills. The mixing model (Figure 3a) indicates leaves may be a primary source of Ca to the stream during low discharge. Indeed, these shallow soils are strongly leached of Ca (< 0.16% wt.; Jin et al. 2010), and organic matter may be a relatively large pool of Ca in this system. In contrast to Shale Hills where Ca trends are strongly influenced by organic matter, Ca at Plynlimon may be linked to groundwater, an effect most pronounced in the Upper Hore. Ratios of Ca:Mg ~~ratios~~ trend towards organic-poor sources at low flow, likely due to inputs of Ca-rich groundwater during base flow that is diluted by increasing contribution from soil water at high flow. Although a lack of groundwater data from these two subcatchments limits our ability to directly assess inputs to the stream, groundwater collected from lower elevations in the Plynlimon forest are rich in Ca and Si (Neal et al., 1997).

Similar to Ca at Shale Hills, K limitation may drive its increased association with organic matter at Plynlimon. Values of $C_K : C_{Na}$ decrease at Shale Hills and increase at Plynlimon with increasing Q in a manner consistent with changing inputs from organic-rich sources (Figure A7). Although geochemically similar, Na is a nonessential element (Kirkby, 2012) that is readily weathered from soils whereas K is a plant macronutrient that accumulates in leaf tissue (Herndon

et al., 2015<u>4</u>). From the mixing diagrams and m_K, we infer that K has a stronger organic control at Plynlimon than at Shale Hills. One explanation for this is that net primary productivity (NPP) is higher (896 g C m^{-2} y^{-1}; unpublished data) but bedrock K is lower (2.90 ± 0.13%; Dere et al., 2013) at Plynlimon than at Shale Hills (NPP = 550 g C m^{-2} y^{-1}; Smith, 2013 and K = 3.76 ± 0.16%; Jin et al. 2010). These data suggest that K is limiting to vegetation at Plynlimon while Ca is limiting to vegetation at Shale Hills due to high demand and low supply.

5   Conclusions

A comparison of ~~two~~ <u>three</u> shale-derived ~~watersheds~~<u>catchments</u>, the Shale Hills CZO in central Pennsylvania, U.S.A. and <u>the Upper Hafren and Upper Hore catchments in the</u> Plynlimon <u>forest,</u> ~~in~~ Wales, U.K., reveals that the concentration-discharge behaviors of elements are strongly impacted by the distribution of organic matter in soils and the hydrologic connectivity of these soils to the stream. At Shale Hills, stream water is derived from organic-rich swales at low flow and then from both swale and planar hillslopes with increasing flow. At Plynlimon, stream water is only dominated by water from organic-rich soils at high flow~~.~~<u>, and contributions from organic-rich upland soils increased following low-land tree harvest in the Upper Hore catchment.</u> Solutes that are limiting nutrients or that are strongly retained by vegetation exhibit non-chemostatic behavior in the stream because they are released to the stream along with dissolved organic carbon. This non-chemostatic behavior is opposite between Plynlimon and Shale Hills due to the different landscape distribution of organic-rich soils. Due to minimal redistribution by vegetation, Na, Mg, and Si are equally concentrated in pore fluids for organic-rich and organic-poor soils, and concentrations of these elements in stream water remain relatively constant. From this, we conclude that the transport of elements associated with organic matter, termed previously as organomarker elements (Hausrath et al., 2009), is strongly controlled by the movement of dissolved organic carbon, leading to a distinct "~~bioactive~~"<u>non-chemostatic</u> behavior in stream waters that contrasts with the "chemostatic" behavior of major weathering elements. Stream chemistry in headwater catchments are variable largely because of the chemical heterogeneities in distribution of organic-rich soils in catchments and how those soils connect to the stream.

Author contributions

EMH, PLS and ALD analyzed the data. EMH prepared the manuscript with contribution from all authors.

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Table 1. Soil profile descriptions and associated SOC (% wt.) and DOC (mM) averages

Site	Category	Horizon	Depth (cm)	DOC (mM)	SOC[b] (% wt.)
Shale Hills[c]					
Planar, valley	Mineral	A	0-15	0.69	4.7
	Mineral	Bw	15-30	0.54	1.6
		Bt	30-53	--	--
		C	53-147	--	--
Swale, valley	Organic	A	0-11	1.28	2.0
	Mineral	Bw	11-38	0.55	1.2
		BC	38-60	--	--
		C	60-178	--	--
Plynlimon[d]					
Peat	Organic	O	0-100+	1.10	40-50
Peaty gley	Organic	O	0-22	1.37	25
	Mineral	Eag	22-37	0.49	5-6
		Bs	37-86	--	--
		C	86-107	--	--
Stagnopodzol	Organic	O	0-19	1.12	46
	Mineral	Eag	19-24	0.35	5
		Bs	24-51	--	--
		C	51-89	--	--

[a] Category (organic or mineral) assigned to soil horizons in this paper; Note that reported SOC and DOC values are averaged over all mineral horizons
[b] Shale Hills SOC estimates from Jin et al. (2010) and Andrews (2011)
[c] Shale Hills soil descriptions from Lin (2006).
[d] Plynlimon soil descriptions from Ruderforth et al. (1984).

Table 2. ~~Shale Hills average chemical data~~Element concentrations (± standard error) in water (precipitation, soil pore water, stream water, groundwater) and vegetation (green leaves, leaf litter) averaged over all available data collected from the Susquehanna Shale Hills Critical Zone Observatory in Pennsylvania, USA between 2006 – 2011

	pH	Na	K	Mg	Ca	Si	Fe	Mn	DOC
		----------------------------------µmol L^{-1}----------------------------------							mmol L^{-1}
Precipitation	4.5	2.1	0.67	0.73	2.65	--	0.24	0.05	0.08[a]
± std. err.	0.2	0.4	0.28	0.16	0.51	--	0.14	0.01	0.02
Soil Pore Water									
SPVF, A horizon	4.5	29	34	62	142	123	0.61	0.38	0.69
± std. err.	0.2	3	3	10	26	5	0.15	0.06	0.06
SPVF, B horizon	4.7	34	29	89	146	125	0.25	0.44	0.54
± std. err.	< 0.1	2	1	8	15	3	0.02	0.05	0.04
SSVF, A horizon	3.9	21	88	39	72	112	1.7	6.8	1.28
± std. err.	0.1	3	14	5	11	11	0.26	1.9	0.33
SSVF, B horizon	4.4	28	29	79	35	126	0.21	1.3	0.55
± std. err.	< 0.1	1	1	2	1	2	0.03	0.1	0.03
Average, all soils		28	45	68	99	121	0.69	2.2	0.77
RSD (%), all soils		19	64	33	55	5	100	140	46
Stream Water									
Low flow	6.3	39	50	162	450	108	14	5.2	0.81
± std. err.	< 0.1	< 1	1	3	10	1	2	0.7	0.06
Moderate flow	5.7	32	31	122	240	101	1.9	1.1	0.45
± std. err.	0.1	1	< 1	3	7	1	0.4	0.2	0.03
High flow	5.9	26	29	96	163	99	0.53	0.33	0.42
± std. err.	0.1	< 1	< 1	2	6	1	0.02	0.03	0.03
Groundwater	--	145	24	404	758	124	0.14	2.9	0.20
± std. err.	--	6	< 1	13	27	1	0.08	0.2	0.05

Vegetation	Na	K	Mg	Ca	Si	Fe	Mn	
	--------------------------------µmol g^{-1}--------------------------------							
Leaf litter	n/a	69	59	263	n/a	n/a	49	
± std. err.		6	3	15			3	
Green leaves	1.1	221	69	186		0.99	42	
± std. err.	0.2	15	7	18		0.06	4	

[a]Andrews et al. (2011)

Table 3. Solute concentrations (± standard error) averaged over all available data collected from the Upper Hore (pre-harvest: 1983 – 2005; post-harvest: 2005 – 2010) and Upper Hafren (1990 – 2010) catchments in the Plynlimon forest in Wales, United Kingdom Plynlimon average water concentrations (µmol L⁻¹) (± standard error)

	pH	Na	K	Mg	Ca	Si	Fe	Mn	Al	DOC
				---------------------------------μmol L^{-1}---------------------------------						mmol L^{-1}
Precipitation	4.98	69.6	2.60	8.52	6.89	2.63	0.19	0.03	0.66	0.045
± std. err.	0.01	3	0.10	0.32	0.59	0.35	0.02	< 0.01	0.05	0.001
Soil Pore Water										
Peat	3.24	143	5.55	27.1	12.6	9.40	2.97	0.16	2.22	1.10
± std. err.	0.10	4	0.54	1.2	0.5	0.38	0.15	0.02	0.20	0.45
Peaty gley organic	3.56	239	29.7	30.0	8.32	47.6	9.29	---	26.6	1.37
± std. err.	0.07	6	3.2	1.0	0.41	2.0	0.42	---	1.3	0.77
Peaty gley mineral	4.16	220	10.2	26.7	5.32	57.1	12.2	---	55.9	0.49
± std. err.	0.01	1	0.2	0.1	0.02	0.3	0.5	---	0.2	0.09
Stagnopodzol O	3.82	165	25.7	29.8	22.7	18.9	4.25	0.27	8.00	1.12
± std. err.	0.07	5	2.3	1.1	1.4	0.7	0.20	0.04	0.38	0.04
Stagnopodzol min	4.12	159	7.91	19.9	11.7	33.7	0.96	0.47	19.9	0.35
± std. err.	0.01	< 1	0.04	< 0.1	0.04	0.2	0.02	0.01	0.2	< 0.01
Upper Hore										
Low flow	6.98	177	3.06	36.1	78.3	63.0	2.59	0.32	3.56	0.10
± std. err.	0.02	1	0.06	0.3	1.0	0.9	0.11	0.01	0.40	< 0.01
Moderate flow	6.01	180	3.11	29.8	39.7	48.4	2.02	0.42	7.44	0.12
± std. err.	0.02	1	0.05	0.1	0.5	0.3	0.04	< 0.01	0.12	< 0.01
High flow	4.75	184	3.78	25.6	17.5	30.4	2.08	0.40	16.2	0.21
± std. err.	0.02	3	0.11	0.5	0.4	0.5	0.07	0.01	0.3	< 0.01
Avg., pre-harvest	5.94	178	3.2	30.1	42.3	47.9	2.03	0.41	8.4	0.13
± std. err.	0.03	1	< 0.1	0.2	1.3	0.4	0.04	0.01	0.2	< 0.01
Avg., p Post-harvest, all flows	5.96	169	8.9	30.2	41.3	45.0	3.33	0.51	7.9	0.31
± std. err.	0.05	1	0.3	0.3	0.7	0.9	0.11	0.01	0.3	0.01
Upper Hafren										
Low flow	6.45	160	2.96	27.8	17.4	67.8	1.21	0.27	2.02	0.08
± std. err.	0.02	1	0.06	0.2	0.1	1.0	0.06	0.01	0.18	< 0.01
Moderate flow	5.79	153	3.52	26.0	13.8	57.7	1.74	0.38	3.51	0.13
± std. err.	0.02	< 1	0.06	0.1	0.08	0.5	0.04	< 0.01	0.09	< 0.01
High flow	4.85	142	5.04	22.8	10.1	34.5	2.68	0.34	7.44	0.24
± std. err.	0.02	2	0.15	0.4	0.2	0.8	0.12	0.01	0.22	0.01
Groundwater	5.26	227	8.7	79	94	86	5.9	2.54	1.86	0.032
± std. err.	0.07	8	1.7	11	20	4	1.5	0.33	0.11	0.002

Table 4. Slopes of regression lines fit to C-Q data (log C = a + m * log Q)

	Na	K	Ca	Mg	Si	Al	Fe	Mn	DOC
Shale Hills (2008 – 2010)									
Slope (m)	-0.04	-0.07	-0.12	-0.05	-0.01	-	-0.30	-0.19	-0.11
Std. Err.	< 0.01	< 0.01	0.01	< 0.01	< 0.01	-	0.01	0.02	0.02
R^2	0.32	0.56	0.43	0.30	0.09	-	0.58	0.24	0.14
Upper Hafren (1990 – 2010)									
Slope (m)	-0.05	0.18	-0.20	-0.08	-0.26	0.58	0.33	0.10	0.42
Std. Err.	0.00	0.01	0.00	0.00	0.01	0.02	0.02	0.01	0.02
R^2	0.20	0.19	0.64	0.27	0.67	0.53	0.26	0.08	0.37
Upper Hore (pre-harvest; 1983 – 2004)									
Slope (m)	0.00	0.07	-0.51	-0.12	-0.27	0.52	-0.05	0.05	0.26
Std. Err.	0.00	0.01	0.01	0.00	0.01	0.01	0.02	0.01	0.02
R^2	0.00	0.04	0.89	0.43	0.75	0.59	0.01	0.04	0.23
Upper Hore (post-harvest; 2005 - 2010)									
Slope (m)	-0.04	0.26	-0.49	-0.11	-0.23	0.42	-0.04	0.12	0.25
Std. Err.	0.00	0.03	0.01	0.01	0.01	0.02	0.03	0.02	0.03
R^2	0.12	0.18	0.90	0.50	0.83	0.68	< 0.01	0.16	0.21

[a]Calculations exclude data where concentrations fell below the detection limit.

[b]All slopes are statistically different from zero ($p < 0.001$) except Na (pre-harvest) and Fe (post-harvest) in the Upper Hore

Figure Captions

Figure 1. Map views of the Susquehanna Shale Hill Critical Zone Observatory (Shale Hills, PA, USA; left) and Plynlimon (Wales, UK; right) catchments. Symbols mark locations of precipitation (black square), stream water (red circle), pore water (black triangle), and groundwater (green circle) samplers. Brown and green shading delineate major landscape features that are organic-rich or organic-poor in each catchment: swale versus planar slopes at Shale Hills or peat versus forested regions at Plynlimon. Notably, the most organic-rich soils are in lowlands in Shale Hills but uplands in Plynlimon; consequently, inputs from organic-rich soils dominate stream flow under low-flow conditions in Shale Hills but high-flow conditions in Plynlimon.

Figure 2. Log C (solute concentration) versus log Q (discharge) in the Shale Hills catchment (a, b) and two Plynlimon subcatchments, the Upper Hafren (c-e) and Upper Hore (f-h). Data from the post-harvest period (2005 – 2010) in the Upper Hore are plotted in separate panels (i-k). For each catchment, the left panel shows elements that exhibit chemostatic behavior, the middle panel shows non-chemostatic elements that exhibit behavior similar to DOC (e.g. dilution at Shale Hills and enrichment at Plynlimon), and the right panel shows elements that exhibit dilution behavior.

Figure 3. Molar ratios of major divalent (Ca:Mg) versus univalent (K:Na) cations are plotted on the left and the molar ratios of Mn (mmol) to Mg (mol) versus dissolved organic carbon (mmol L^{-1}) are plotted on the right for solute source pools in the forested Shale Hills (a, b), peatland Upper Hafren (c, d), and predominately forested Upper Hore (e, f) catchments. Arrows indicate direction of increasing discharge for average stream chemistries. Values for total C (~ 33 mmol kg^{-1}) and K:Na (~60) in leaves are divided by 10 to fit on plots (a) and (b). For soil pore water, filled symbols indicate organic-rich waters and open symbols indicate organic-poor waters.

Figure 4. The degree of non-chemostatic behavior for a solute in stream water, denoted by m_j, was correlated with the relative concentration of that solute in organic-rich soil water in each catchment. Specifically, m_j was **(a)** negatively correlated with the ratio of solute concentrations in organic-rich versus organic-poor soil waters at Shale Hills ($R^2 = 0.90$, $p < 0.001$) and positively correlated with the ratio of solute concentrations in pore waters versus precipitation in **(b)** the Upper Hafren ($R^2 = 0.48$; $p < 0.05$) and **(c)** the Upper Hore ($R^2 = 0.42$; $p < 0.05$). Error bars represent the standard error of each value and are smaller than the symbol where not visible.