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 chemostatic elements; 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:

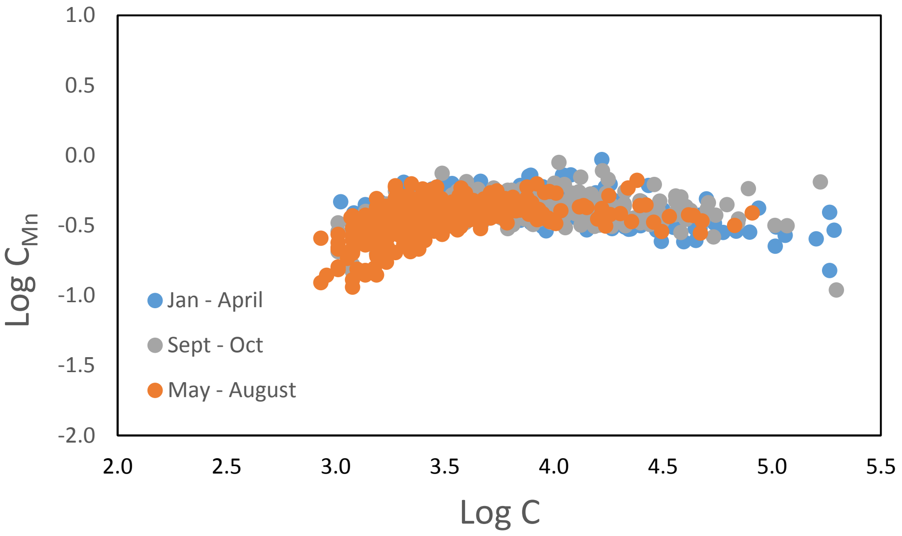
1 **-** The authors discuss the seasonal variations in element concentrations, discharge patterns, and precipitation regimes. These seasonal variations are then used to support seasonally dependent conceptual models (for example, page 226, section 4.1, lines 4-8). However, the C-Q regression analyses 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).



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: