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Discussions

Interactive comment on "Biotic controls on solute distribution and transport in headwater catchments" *by* E. M. Herndon et al.

Anonymous Referee #1

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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.

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.

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

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

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.

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.

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.

1. Introduction

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?

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.

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.

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

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

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?

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 carbon-related compounds? I believe so.

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

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

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

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

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.

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.

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…"?

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?

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.

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

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

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

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.

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

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).

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

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.

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

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.

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.

References

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

Figures and Tables

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

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

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?

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

Technical corrections

1. Introduction

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

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

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

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

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

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

2. Methods

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

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.

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

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

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

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

4. Discussion

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

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

References

Please, include all the missing references.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 12, 213, 2015.