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Hydrology and Earth System Sciences Discussions

Interactive comment on "Spatial and temporal dynamics of stream chemistry in a forested watershed impacted by atmospheric deposition" *by* K. B. Piatek et al.

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Title: Spatial and temporal dynamics of stream chemistry in a forested watershed impacted by atmospheric deposition.

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General Comments

This paper examines stream chemistry and natural isotope abundances at nine tributary sampling locations within a 135 ha watershed with varied topography and soils. The authors attempt to elucidate the terrestrial biogeochemical and hydrologic processes that impact stream water quality by determining solute concentrations during varied flow regimes over a two year period. While this paper would be a good contribution to Hydrology and Earth System Sciences there are some issues that need to be addressed before it can be published.

While there is no question that this watershed has been impacted by atmospheric deposition the focus of this paper is not in this subject area. The title should be modified to reflect the overall objective as stated by the authors, "to better understand factors responsible for solute dynamics". The study presents an impressive array of data and much of the results and discussion sections focus on the relationships displayed in Figures 3 and 5. I am not able to understand why the points plotted in the graphs of these two figures are not identical with only different symbol coding dependent on whether the space (locations) or temporal (discharge periods) relationship is being examined. Can this be clarified? In some cases the authors refer to the solute relationships as "increasing" or "decreasing" and in other cases make note of r2 values, however not all relationships show regression lines in the figures. It is not stated if the absence of a regression line indicates absence of a relationship and for some graphs it appears that significant relationships may exist. The authors need to clarify which relationships are statistically significant and which are not in the manuscript text and the figures. The authors will also need to address some situations where figures do not contain data that is referred to in the text and other cases where the data presented does not appear to support their discussion. I have also included some specific suggestions and questions that elaborate on my general comments above with the hopes that they may benefit the authors.

Specific Comments

Introduction

Page 2583, Lines 22-24. May also be low solute concentration due to the lack of a hydrologic connection between terrestrial and aquatic system.

Page 2584, Lines 11-13. Add additional background information regarding S deposition and brief definition of stage 1 of N saturation or perhaps delete statement from the text.

Page 2584, Line 23. I would have thought that nitrification rates would be high in the summer but that uptake and immobilization would also be high resulting in low exports from the upper soil profile.

Page 2585, Lines 15-18. What about the other year used in the analysis? Perhaps a more general statement about the study time frame and then the specific hydrologic conditions encountered would give the reader the broader context.

Methods

Page 2585, Line 26. Insert "composed of up to".

Page 2585, Line 18. Replace "buy" with "by".

Page 2587, Line 5. Insert "at the H-flume at the watershed outlet (S2) weekly".

Page 2589, Lines 18-21. Have also included NO3- graphs and discussion includes NO3- as key source indicator for mineral soil and forest floor.

Results

Page 2590, Lines 21-22. Text reference here is "simplified" model however Table 2 caption notes "full" model and Methods section 2.4 describes the "reduced" model. Need to correct/standardize.

Page 2591, Line 4. Statement not supported by data in Table 3. Mg greater at S15 than at other locations but still only 25

Page 2592, Lines 9, 14. Relationships with Cb not shown in Figure 3 but referred to in text.

Page 2592, Lines 17-18. DOC results should be moved to previous paragraph but this statement also repeats general ideas stated re: DON/DOC in Lines 12-13.

Page 2593, Line 8. "Silica concentration ....." should be moved to Methods section.

Page 2593, Line 18. Insert "high variability within each sampling period".

Page 2593, 2594, Section 3.5. pH and DON relationships not shown in Figure 5 but referred to in text. These relationships also referred to in the Discussion section of the paper.

Page 2593, Lines 22-23. Does variation "across space" refer to variation between locations at discuss in Section 3.3? or something else? Please clarify this statement.

Page 2594, Line 1. This statement appears to repeat Page 2593, Lines 25-26; also the increase in NO3- during the spring in Figure 5 is greater than during the winter.

Page 2595, Section 3.7. Need to clarify this section, Table 6 and stated Methods section 2.7. Methods stated exclusion of year and location in this analysis but year is included here. What is the significance of year in the analysis when methods state that analysis includes only specific discharge periods selected from the two years?

Discussion

Page 2595, Line 25 and Page 2596, Line 1. No regressions are shown for these "strong relationships". Should refer to Figure 3 rather than Figure 2.

Page 2596, Lines 11-17. Rewrite this section to clarify. Some contradiction in statements that dry spells are not common but that drought may be experienced more commonly.

Page 2596, Line 27 to Page 2597, Line 6. Some elements of this discussion are quite speculative. Are there quantitative measurements of the overstory vegetation at S14 and S15 or even throughout the entire watershed? or the parent material chemistry? As mentioned above Ca is the dominant cation at S15 not Mg as stated, although Mg

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is greater than at other locations. Could you provide some elaboration of the role of sugar maple litter in high nitrification rates?

Page 2596, Lines 9-11. In the previous paragraph you attribute high NO3- to vegetation differences. Can you explain in more detail why the high elevation areas are more conducive to high rates of nitrification?

Page 2597, Section 4.1.1. Some clarification needed here. Up to this point in the paper you have made an effort in explaining why stream chemistry at the sampling locations are different, and now you are sort of saying that things are the same. Agree with your final sentence and the wetland immediately above S2 is a good example of this; higher DOC, lower NO3-. Also, specifically define "solutes originating from groundwater", lines 19,20.

Page 2598, Line 23. Replace "storms" with "fall".

Page 2599, Lines 15-27. Does this relationship depend on whether the fall is wet or dry? It appears that the discharge of NO3- from the soil carries to the melt period as this period has the highest concentration as shown in Table 4.

Page 2600, Lines 5-6. What do you mean by "patterns represent marked changes"? Is this in comparison to "normal" years or something else? Please provide more detail around this statement.

Page 2600, Section 4.4.2. While the relationships established between terrestrial sources and solute generation are well outlined in this section and throughout the manuscript I do not find that Figure 6 provides a very useful representation. The two diagrams are identical with the exception of a few flow arrows during the high flow period. I think this kind of figure is a good idea but also think it requires some more detail and explanation.

Conclusions

Page 2602, Line 8. The paper has not associated the sampling locations with "vegetation and topographic attributes" in a comprehensive, quantitative way but rather has inferred terrestrial processes and solute sources from stream chemistry. Modify this portion of the text.

Technical Corrections

The use of "cations" and "Cb" is confusing in many instances in the paper (e.g. Page 2592, line 14, "Across the watershed, cations, Cb, ...were negatively related.....". I would suggest that the authors standardize with one term or the other and also refer specifically to Ca or Mg when they are referring to these solutes.

Tables and Figures

Table 5. Delete n.s. in DOC column of daily discharge

Table 6. Add more detail to the table caption to inform reader of years, discharge periods that are analyzed.

Figure 1. X must represent stream sampling locations; note this in the legend. Add X for S11, delete X's at 748m and 634m marks. Delete groundwater sampling locations as this data is not provided in the paper

Figure 3 and Figure 5. These figures should be presented in the same manner with the same variables for greater ease of interpretation by the reader. Suggestions: include either Cb for both figures only or Ca and Mg for both figures; group plots according to Cb (Ca, Mg) vs Si Al DOC, SO42- vs Si Al DOC, NO3- vs Si Al DOC, pH vs Si Al DOC, DON vs Si Al DOC, DOC vs Si Al, Al vs Si, NO3- vs Cb (Ca, Mg) SO42- NH4+ ; group plots to combine common x-axis and legend across several plots; standardize presentation of regression lines (may be more useful to add an additional table with r2 and p values)

References

I am most familiar with similar work done in a hardwood forest at the Turkey Lakes

Watershed (TLW) in central Ontario. Some potential references to support your results for your consideration from the TLW study.

Atmospheric/terrestrial NO3-

Spoelstra, Schiff, Hazlett, Jeffries, and Semkin. The isotopic composition of nitrate produced from nitrification in a hardwood forest floor. Geochimica et Cosmochimica Acta 71: 3757-3771, 2007.

Spoelstra, Schiff, Elgood, Semkin, and Jeffries. Tracing the sources of exported nitrate in the Turkey Lakes Watershed using 15N/14N and 18O/16O isotopic ratios. Ecosystems 4, 536-544, 2001.

Drought/stream SO42-

Schiff, Spoelstra, Semkin, and Jeffries. Drought induced pulses of SO42- from a Canadian shield wetland: use of 948;34S and 948;18O in SO42- to determine sources of sulfur. Applied Geochemistry 20, 691-700, 2005.

Soil processes/stream solutes

Hazlett, Semkin, and Beall. Hydrologic pathways during snowmelt in first-order streams at the Turkey Lakes Watershed. Ecosystems, Volume 4, Number 6: 527-535, 2001.

Hazlett, English, and Foster. Ion enrichment of snowmelt water by processes within a podzolic soil. Journal of Environmental Quality 21 (1): 102 109, 1992.

Wetlands/stream DOC

Creed, Sanford, Beall, Molot, and Dillon. Cryptic wetlands: integrating hidden wetlands in regression models of the export of dissolved organic carbon from forested landscapes. Hydrological Processes 17, 3629-3648, 2003.

Thank you for the opportunity to review this paper.

Paul W. Hazlett Forest Soils Scientist

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 5, 2581, 2008.

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