

Hydrol. Earth Syst. Sci. Discuss., 5, S1565–S1569, 2008

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

Anonymous Referee #1

Received and published: 23 October 2008

MS-NR: hessd-2008-0109, version 1

Title: Spatial and temporal dynamics of stream chemistry in a forested watershed impacted by atmospheric deposition, by K. Piatek, F. Christopher, and J. Mitchell.

General comments

This paper presents results of the variation of stream solute concentrations in space and time as measured at eight sampling locations in a 135-ha watershed over a two-year period. In my opinion, the questions addressed are relevant for HESS readers

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and sufficient analyses and ideas are presented. While the introduction and methods are well written and clear, the presentation of the results should be improved before considering publication. This e.g. holds true for the the temporal relationships among solutes, because the text does not clarify whether relationships were statistically significant and sometimes appears to contradict the corresponding figure. All figures should be updated too, and it might be valuable to consider a more advanced graphic program than is currently used. The discussion is well written, but could be more cautious on some points. For example, I am not sure whether the spatial and temporal dynamics of N cycling at the watershed level can be evaluated based on the presented streamflow chemistry only.

Specific comments

- p. 2588 line 20: were any (international) standards used for d15N-NO₃-. Please add the quality of the laboratory measurements compared to the standard (for d18O, and if possible, for d15N).
- p. 2589 line 20: Please add which functional forms of relationships were tested. Fig. 3 and 5 generally indicate single linear regressions, but for some solutes other relationships were graphed (e.g. Fig. 5, SO₄²⁻ vs NO₃⁻ for spring).
- p. 2590 line 19-20: Only for TN and DOC, statistically significant differences between the two sampling years were found. Why then is "year" not a significant factor in the ANOVA (Table 2) for these solutes?
- p. 2591 line 1: what exactly is meant by the "sum of base cations"? If I am correct, K⁺ and Na⁺ were not measured in the water samples (cf. p. 2587 line 23). So the sum of base cations in this study is actually the sum of Ca²⁺ and Mg²⁺? Why is the sum of base cations then different from the sum of Ca²⁺ and Mg²⁺ in Table 3?
- p. 2593 line 11-16: with respect to the temporal differences in isotopic NO₃⁻ values, now only the p value for the general time effect is given (p = 0.0015). Please add for

which periods the delta values differed significantly.

- p. 2593-94, 3.5: for most of the relationships mentioned in this section, it is difficult to understand whether the relationship was statistically significant. E.g., p 2593 line 26 states that "nitrate increased with Si concentrations in all periods but snowmelt", while in the corresponding Si-NO₃- graph in Fig. 5, only for the spring period a regression line with R² is shown; furthermore, visually, it appears unlikely that there would be a significant relationship for e.g. the summer period. Similar remarks apply to relationships between many other pairs of solutes (e.g. Al-NO₃-: no regression line in Fig. 5 despite p. 2594 line 7). So, the whole section on temporal relationships should be improved to clarify whether the stated relationships were statistically significant or not. This could be done by adding R² and/or p values in the text or in a separate table.

- p. 2594 line 23, p. 2594 line 5: "cations including Cb", is this NH₄⁺, Ca²⁺ and Mg²⁺? If so, I think it is better to mention these specific ions.

- p. 2594 line 26: "NO₃- was significant in every sampling location": rephrase to clarify what exactly was significant

- p. 2597 line 10: why is high elevation conducive to high rates of nitrification? Please explain and/or add references.

- p. 2599 line 6-27. It might be good to add that NO₃- is not only taken up by plants or microbes but also immobilized abiotically in soils.

- Discussion section: the division of the discussion should be improved. Now, the discussion is divided into two major sections (spatial patterns 4.1; temporal patterns 4.2). However, in 4.1 there is only one subsection (4.1.1), while the second subsection of 4.2 (conceptual model) covers both space and time.

- p. 2602 line 10: in my opinion, the conclusion on nitrification in fall is stated more strongly than can be justified by the presented data.

- Table 2 to 6: why is NH₄⁺ not mentioned in these tables and figure, while this solute

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was measured (and results were were given in Fig 3 and 5)?

- Fig. 2 and 4: please provide correct axis legends with units, e.g. $\delta^{15}\text{N-NO}_3^-$ in promille. Please add some measure of variation on each data point to the graph (e.g. standard deviation in O and N isotope derived from laboratory performance, or actual standard deviation on the measurements). In this way, it would be more clear how important the differences between periods or sampling points are (cf. p. 2592 line 14-15 natural abundance isotope values of N and O in NO_3^- were not significantly different for sampling points).

- Fig. 6: as the two figures are the same, except for some arrows, the lowest figure could be used only, with some explanation in the legend. However, I found the figure less informative than e.g. Fig. 3 and 5. If the figure would be kept in the paper, please use the same font within one figure.

Technical corrections

- p. 2586 line 10: please add the author name of each plant species (e.g. *Fagus gradifolia* Ehrh.)

- p. 2586 line 18: "buy" should be "by"

- p. 2591 line 26: here "Cb" is mentioned for the first time in the text (without mentioning the full term). Please abbreviate a term at its first appearance (so on top of this page), and use the abbreviation consistently.

- p. 2592 line 16: "nor" likely should be "not"

- p. 2600 line 13-19: this is a single-sentence paragraph. It would be easier to read if split up in several sentences.

- p. 2601 line 10: I guess a "-" is missing after "S15"

- Table 2 to 6: please add explanation of "Cb"

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- Fig. 1: what are the x symbols given at 748 and 634 m?
- Fig. 3 and 5: please provide units of the solute concentrations (in axis legends or at least in the figure caption), and mention the charge of ions (which are now sometimes lacking for Mg^{2+} , Ca^{2+} en NO_3^-)
- Fig. 4: Caption: "values" should be "Delta values"
- Fig. 5: p. 2621: graph of Ca^{2+} vs NO_3^- : data points and legend are overlapping

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