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Hydrology and Earth System Sciences
Discussions

Interactive comment on "Antecedent flow conditions and nitrate concentrations in the Mississippi River Basin" *by* J. C. Murphy et al.

Anonymous Referee #1

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The paper "Antecedent flow conditions and nitrate concentrations in the Mississippi River Basin" by J. C. Murphy, R. M. Hirsch, and L. A. Sprague presents an analysis of the variability of nitrate concentration in streams vs antecedent flow conditions using time serie statistics.

The impact of antecedent hydrological conditions on water and nutrient flow in watersheds is of course of interest for HESS, and a great amount of litterature has been published in this area in the past 40 years. However, I feel that the novelty brought by this paper is not evident and its quality needs major revisions to reach the standard expected for HESS.

1- First, the short literature survey is about studies on correlations between antecedent

moisture (or hydrological) condition and nutrient export, while the analysis here is about antecedent flow conditions. The authors are jumping from moisture to flow without discussing the possible differences between them. Only in "methods" section, p 11455 line 21 the authors claim that "Q ratio serves as a surrogate for overall basin wetness or dryness", but there is no discussion about the implication of this. More generally, the use of hydrological terms is very loose: for example high flow and storm events are different concepts, but apparently are used here as equivalent. Up to the point that in the result and discussion section (p11459), it is said that "the strenght of the relashionship shown here (table 2) are weaker than those reported elsewhere", but the litterature cited refer (for the papers I kown at least) to analysis at the scale of individual storm events, which is of course not at all the same.

2- The authors should clearly distinguish what, in their statistical methodology, is taken from previous papers and what part (if any) is novel. If I understand (but I am not sure), the novelty is that they correlate Q ratio with NO3 anomaly (CA). Is there a possibiliy that the (very poor) correlation found in some cases between these two variables could be due to the fact that they both include stream flow data in their calculations? There is no discussion on the rationale, interest and possible drawbacks of the methodology. For example, it is said that (p11457, line 6) the "nitrate anomalies can be conceptualized as the portion of the concentration signal that is not accounted for by contemporaneous discharge, season or long-term trend". But what part of the anomaly could have other origin, like measurement or model errors for example?

3- The rationale of the method is also missing. For example why is Q ratio calculated for the previous 364 days? What would be the implication of using shorter or longer periods? Is it based on the implicit assumption that the stream chemistry only results from the conditions of the current year? Or, in other terms, that the system is "source-limited"? If so, this should be explained and discussed considering relevant literature (see below).

4- My most serious concern is about the conclusions drawn from the statistical analysis in terms of real word processes. First, the authors should track and remove from the text all the words that imply causality, when they are showing only correlations, e.g. p11458 line 8 “to quantify the effect of antecedent flow on nitrate concentration”, but they are many more. Only at the end of the paper (p11469), it is said “While this study identifies significant relationships between antecedent flow conditions and nitrate concentration, it does little to explain the cause of these relationships”, but the whole result and discussion section is in contradiction with this statement. There would be much to say about the conclusions that are drawn from the results in terms of hydrological processes; I will take only two examples. First example, the impact of drought on crop yields can of course increase the nitrate content of soil. But is antecedent flow conditions a good surrogate for crop water stress? A rainy winter, leading to high stream flows, can be followed by dry spring and summer, and in this case, you will have a high Q ratio but a high water stress for crops. This should at least be discussed. Second, there as been a great deal of literature in the past 20 years, demonstrating that the chemical signature of the stream is a complex mixing of water with a large spectrum of residence time, from days to decades, (see for example Kirchner et al., 2001, JoH, see also the recent review of the PUB decade by Hrachowitz et al. 2013, in Hydrological Sciences Journal; but they are many more). The transport from soil to stream can take much more than a year. As another recent example, Gascuel et al, 2010, Science of the total Environment, have shown that climate can influence the mixing of groundwater of different residence time which results in variations in nitrate concentration in streams. All these studies demonstrated that in many cases, the hydrosystem is transport-limited rather than source-limited. This needs to be discussed and conclusions in terms of proceses should be drawn with much more caution.

To improve this paper, I would suggest that the authors rework their paper structure: i) introduction should be improved, by focusing on the interest of the method with respect to the existing literature, ii) method section should describe the rationale of the method, and remove trivial content (like all paragraph p 11456, lines 3-19, and figure2) iii) result section should be separated from the discussion, redundancies between text and fig-

ures should be removed. I don’t see the interest of Figure 2, but a figure showing the evolution of Qr and CA with time, for few contrasting years, could be interesting; iv) the discussion section should be divided in 3 parts, one discussing the interest and limits of the method, the second discussing the results for the different sites and periods and the third speculating about possible mechanism involved, but including reference to recent litterature on the processes involved in nutrient transport from soils to stream. The section 4.3.4, about provisional results of 2013, should be considerably reduced, or removed, or if the results are now established, be included in the whole analysis.

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., 10, 11451, 2013.