Author response

Antecedent flow conditions and nitrate concentrations in the Mississippi River Basin.
J.C. Murphy, R.M. Hirsch, and L.A. Sprague
December 22, 2013

We thank the two anonymous referees for their time and effort spent reviewing our manuscript and providing constructive feedback. Their thoughtful comments led us to address a number of important issues and clarify our message. We also thank the Editor for the opportunity to make these changes and resubmit.

Both referees stated we needed to provide a more thorough explanation for why we chose to calculate the Qratio using the previous year's flow.

> ***Referee 1* – "The rationale of the method is also missing. For example why is Q ratio calculated for the previous 364 days?..."**
>
> ***Referee 2* – "No clear rationale is given why the authors chose one year to describe antecedent flow conditions (p. 11455). Was this decision based on testing conceptual considerations?..."**

Streamflow is known to vary by season at the eight sites in our study (for example, highest flows typically occur during the spring). Therefore, we used the previous year to calculate antecedent flow conditions primarily because using this method makes Qratio a random variable for which the distribution does not change with time-of-year. To further elaborate on our choice of the Qratio the following paragraph has been added to the methods section:

"By using streamflow integrated over the year as a large-basin surrogate for the kinds of hydrologic storage and flux measures that might be used in small-basin-process models we are able to acquire a general measure of basin moisture that is likely related to other physical, chemical and biological processes in a basin that are affected by preceding moisture conditions. The choice of a one year averaging period used to compute the Qratio makes this antecedent flow measure independent of the time of year and season. It is possible that more complex statistical formulations with seasonal terms or an averaging period other than one year would have a stronger statistical association with nitrate anomalies, but model parsimony led us to commit to this simpler formulation. Using Qratio to describe antecedent flows characterizes hydrologic conditions broadly and allows for an initial examination of how nitrate concentration responds following a drought or high flow period. If significant relationships are documented, future studies can help better define the specific hydrologic processes that influence nitrate concentration during and after a drought or high flow period."

Responses to specific referee comments are presented below.

--- Referee #1

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 series 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 literature 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.

We feel the novel aspect of our manuscript is the exploration and identification of relationships between a measure of antecedent flow and nitrate for very large basins. While small scale studies have identified the influence of climate variability or antecedent moisture/flow on nitrate either during storm events or more generally, our study is one of only a few to identify such relationships in regional-scale basins (about 30,000 to 600,000 square kilometers (km^2)). Interestingly, referee 2 agrees with us: "…the novel aspect of the study in my opinion [lies] mainly in the large scale of the study area…". To further emphasize the novelty of our study we have added (1) a paragraph to the introduction that discusses the complicated processes that occur in very large basins and how to work within these constraints, (2) a site description section that further elaborates on the theme of large-scale basins by discussing the diversity of climate and basin characteristics for the eight large-scale basins in our study, and noting that all but two of the cited studies in our manuscript consider basins of less than 1,000 km^2 with one of the two larger-scale studies considering basins ranging from 114 to 117,400 km^2 and the other considering a single basin of 8,900 km^2, and (3) additional text throughout the manuscript that further reiterates this large-scale-basin theme.

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.

Referee 2 stated in their comments, "such [large] basin sizes require the development/use of integrating measurement proxies, here river flow conditions for soil moisture…"— this is exactly the reason we are using streamflow (Qratios) as a surrogate for overall basin moisture conditions. Large basins contain a diversity of climatic, geologic, and land use conditions in addition to substantial spatial variability of precipitation inputs which result in some portions of a basin experiencing very wet conditions while other portions of the basin experience average or even very dry conditions. Since large spatial scales result in highly variable soil water and groundwater storage (spatially and temporally), antecedent moisture conditions in large basins are likely best defined by well-integrated measurement proxies that amalgamate these variable conditions. To make this connection more explicit we have incorporated additional text into the introduction and methods sections. For example, near the end of the introduction we added this statement: "Since large spatial scales result in highly variable soil water and groundwater storage (spatially and temporally), antecedent moisture conditions in large basins are likely best defined by well-integrated measurement proxies that amalgamate these variable conditions. In this study we use antecedent streamflows at the downstream end of a basin as a proxy for basin-wide antecedent soil moisture."

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 strength of the relationship shown here (table 2) are weaker than those reported elsewhere", but the literature cited refer (for the papers I known at least) to analysis at the scale of individual storm events, which is of course not at all the same.

Thanks for making a note of this, we realize now that our use of the terms "storm events" and even "base flow" was not well founded since we did not perform a hydrograph separation on our streamflow data. We have removed this terminology from our manuscript and replaced it with the more the accurate terms "mid-high and high contemporaneous flows" and "mid-low and low contemporaneous flows" where appropriate.

As for the phrase "the strength of the relationships shown here (Table 2) are weaker than those reported elsewhere…", we have reworded this phrase to, "…the relationships between antecedent flow and nitrate shown here are weak to moderately strong with low to moderate correlation (Table 2) which is not necessarily surprising given the complexity of solute behavior in large basins...". As noted by the referee, this rewording is more accurate.

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 possibility 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?

Referee 2 states, "A previously developed and separately published regression model is used to predict riverine nitrate concentrations." This is exactly the portion of our methods that comes from a previous publication. We added some text to clarify that the model was published elsewhere and it is the residuals of this model are what we are using in this study. Furthermore, as Referee 2 also states, "Concentration anomalies … are investigated for systematic bias depending on river flow conditions." Relating nitrate anomalies to Qratios at the eight sites in our study is unique to this study. However, we believe the novelty in our paper also lies in the investigation of nitrate anomalies and antecedent flow conditions at a large scale, which has been largely uninvestigated. It is unlikely that the correlations between Qratio and nitrate anomaly are due to the fact that streamflow was used in their calculations. In particular, nitrate anomaly is calculated by subtracting out the portion of the concentration signal that can be accounted for by daily streamflow.

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?

Since the nitrate anomalies are the residuals from a statistical model (WRTDS), there definitely remains a substantial amount of unexplained variation in the concentration estimates, as is the case for modeling approaches in general. The equation for this statistical model, in its original form, includes this random (error) component; however the original presentation of the modeling approach did not incorporate a detailed analysis of this component (see Hirsch et al., 2010. Weighted regressions on time, discharge, and season (WRTDS). *Journal of the American Water Resources Association* 1-24). We have added a sentence to the manuscript (shortly after equation 3) that clarifies this point. "Since nitrate anomalies are simply the residuals from the model these values represent a combination of measurement error, inadequacies of the model's functional form, estimation error of the coefficients, and the influence of other variables that are not considered by the model. In this case, we explicitly consider the role that antecedent streamflow, a variable not included in the model, might play."

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).

This comment is addressed above.

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.

We agree and have refocused the results and discussion so the text discusses only the correlations and removes references that imply causality.

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.

Referee 1 brings up an important point that the antecedent flow statistic we choose to use in this analysis does not consider the timing of wet or dry conditions in the basin. More complex descriptors of antecedent conditions could be developed, but they would greatly add to the complexity of the analysis. As discussed in the introduction, we chose a very simple descriptor of antecedent flow conditions, recognizing that it may miss some of the details of basin responses to particular patterns of antecedent moisture, but we believe that our more parsimonious approach is the right place to start. Determining a good large-basin surrogate for antecedent moisture or crop water stress is complicated by the scale, diversity and variability of land-use, climate and geophysical characteristics of large basins. We added text throughout the manuscript to better articulate this, such as in the methods section, "It is possible that more complex statistical formulations with seasonal terms or an averaging period other than one year would have a stronger statistical association with nitrate anomalies, but model parsimony led us to commit to this simpler formulation."

Second, there has 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 processes should be drawn with much more caution.

Thanks for bringing this to our attention. We have incorporated references to the concepts of residence time and the influence of groundwater on in-stream nitrate concentrations in several places throughout the report, such as when discussing the lack of significant relationships in large basins in the "Nitrate anomaly and antecedent flow across all contemporaneous flows" sub-section: "Further complicating factors include lag-times associated with groundwater discharges (Sanford and Pope, 2013) and the travel time of water through basins (Krichner et al., 2001) and large river networks. For example, at the outflow of the Mississippi River (MISS-OUT), streamwater from different locations in the MRB can take weeks to months to reach MISS-OUT (Nolan et al., 2002), thus the relationships between antecedent flows and nitrate anomalies observed upstream in more homogenous tributaries are likely smeared as water moves downstream and mixes with water from other sources. Also, transport processes in some basins have been found to be more dependent on the permeability and storage capacity of the soil and bedrock as compared to other basins where flow-path lengths and the density of drainage networks are important influences (Hrachowitz et al., 2013)." We added some additional discussion in "Relationships at low and mid-low contemporaneous flows" sub-section, such as: "Other studies of meso-scale basins (<1,000 km^2) have found that, when not considering storm flows, inter-annual variations in climate act as a hydrologic driver that influences the mixing of groundwater with different residence times (but rather stable nitrate concentration) resulting in variations of nitrate concentration and flux in streamwater (Gascuel-Odoux et al., 2010). In this context, the significant relationships during mid-low and low contemporaneous flows suggests the groundwater systems for GRCH and MISS-OUT may be influenced by annual variations in surface conditions or climate. However, the age of groundwater discharge to large rivers can be highly variable depending on geology, terrain and soil characteristics (Sanford and Pope, 2013). Throughout the MRB, the lack of statistically significant (Table 3) or visually strong (Fig. 4) relationships between antecedent flow and nitrate anomaly at mid-low and low contemporaneous flows may simply indicate that there is no overland flow flushing stored nitrate to the river during these flow conditions. However, it may also imply that surface runoff (overland flow) and shallow groundwater with residence times less than one year are likely the main pathways influenced by antecedent flow conditions."

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,

The introduction has been reworked. We moved the paragraph about soil nitrate accumulation following a drought to the end of a new "Study area description" section and developed a new paragraph in the introduction that focuses on exploring hydrologic processes at large scales. The addition of this new paragraph helps to better frame our study and more clearly articulates the novel aspects of our work. However, we respectfully disagree that the focus of the introduction should be on our method but we did include some new text in the introduction (and methods) that more clearly articulates why we used antecedent streamflow as a proxy for basin-wide antecedent soil moisture. For example in the introduction we state, "Since large spatial scales result in highly variable soil water and groundwater storage (spatially and temporally), antecedent moisture conditions in large basins are likely best defined by well-integrated measurement proxies that amalgamate these variable conditions. In this study we use antecedent streamflows at the downstream end of a basin as a proxy for basin-wide antecedent soil moisture."

ii) method section should describe the rationale of the method, and remove trivial content (like all paragraph p 11456, lines 3-19, and figure2)

We agree. We have provided a more thorough explanation of our method, particularly with respect to our decision to use the Qratio as our measure of antecedent flow, and removed the redundant material (text and figure 2) pertaining to how the Qratio varies with different flow conditions the previous year at the VALL site on the Illinois River.

iii) result section should be separated from the discussion, redundancies between text and figures 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;

We removed figure 2, however we respectfully disagree that the results and discussion need to be separated. The results are concisely presented in Tables 2 and 3 and a reiteration of this material in a results section would produce a short, repetitive section. We feel our incorporation of the results and discussion more concisely presents this material. Additionally, a combined results and discussion section is not uncommon for other papers published in HESS.

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 literature on the processes involved in nutrient transport from soils to stream.

We respectfully disagree about reorganizing our discussion section. As organized, the Results and Discussion section presents relevant information about the results and corresponding interpretations for our sites and analyses. We feel the suggested reorganization would confuse readers as the interpretations from our three analyses (relationships using all contemporaneous flows together, relationships by flow class, and the translation of nitrate anomalies to percent increases and decreases) would be presented in a single sub-section instead of three separate sub-sections as they are presented currently. However, we have incorporated more relevant literature that addresses the influence of antecedent flow (or moisture) or climate variability on nitrate in large basins. For example in the results and discussion section ("Nitrate anomaly and antecedent flow across all contemporaneous flow" sub-section) we included some discussion on the influence of variable precipitation patterns in large basins on the transport of nitrate to the stream, "… during the 2011 Missouri River flood the upper reaches of the basin provided most of the flood water and this area has very limited row-crop agriculture and thus the water delivered to streams in this region has relatively low concentrations of nitrate; however, most high flow events in the Missouri River basin tend to originate in lower portions of the basin that are highly agricultural and deliver relatively high concentrations of nitrate to streams (Kalkhoff, 2013)." Furthermore, we provide additional text in the mid-low to low contemporaneous flows sub-section about the influence of baseflow and travel time on these results, such as, "In this context, the significant relationships during mid-low and low contemporaneous flows suggests the groundwater systems for GRCH and MISS-OUT may be influenced by annual variations in surface conditions or climate. However, the age of groundwater discharge to large rivers can be highly variable depending on geology, terrain and soil characteristics (Sanford and Pope, 2013)."

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.

We have considerably reduced this section but decided to leave it in the manuscript as this section provides a rudimentary validation that the relationships we identified in our study correspond to observed hydrologic processes and it also points to the important implications that these antecedent conditions can have on practical water supply management issues.

--- Referee #2

The manuscript "Antecedent flow conditions and nitrate concentrations in the Mississippi River Basin" presents and discusses a statistical analysis of the variation of riverine nitrate concentrations depending on antecedent flow conditions at a range of 8 sites within a large-scale river basin. A previously developed and separately published regression model is used to predict riverine nitrate concentrations. Concentration anomalies, i.e. predicted deviations from long-term observations, are investigated for systematic bias depending on river flow conditions.

The manuscript is generally well-written and clear, and the study topic is relevant for publication in HESS, with the novel aspect of the study in my opinion lying mainly in the large scale of the study area: on the one hand, such basin sizes require the development/ use of integrating measurement proxies, here river flow conditions for soil moisture, on the other the conclusions drawn from such studies can lead to insights not easily inferable at smaller scales, here the effect of river eutrophication on marine environments. However, the study in my opinion in some parts lacks a necessary consideration of just these large-scale issues, starting with the introduction, which focuses on smaller-scale experiments, but also later on when the – partly weak – correlations are presented and discussed.

We agree that our manuscript could better address large-scale issues, particularly because this is the novel aspect of our work. The introduction has been reworked to better highlight this important aspect. We moved the paragraph discussing the accumulation of nitrate in soil following a drought to a different location in the manuscript and added a new paragraph to the introduction that discusses issues with exploring hydrologic processes in large basins. This new text leads to a clearer articulation of why we chose to use the Qratio as our measure of antecedent moisture. We believe the revised introduction better sets up the rest of our manuscript.

Also, we added text to the results and discussion section that reiterates our large-scale theme, for example, "The lack of an apparent relationship at HERM, THEB or MISS-OUT is not necessarily surprising given that these sites have drainage areas in excess of 1 million km^2 whereas other sites have drainages areas less than 600,000 km^2. The diversity of basin characteristics in the drainage area above

HERM, THEB and MISS-OUT is very substantial and the Qratio is likely a poor indicator of the moisture status of the particular areas in these basins that are major contributors of nitrate to streamwater."

In my opinion, the m/s would very much benefit from revisiting some of the points raised by the authors themselves in the conclusions on page 11469. Investigating e.g. some simple relationships between catchment properties and nitrate measurements as well as regression results could reveal some clues on where the statistical relationships actually could imply causality, but I would like to leave the decision if such an extension is necessary for acceptance of a revised m/s to the editor.

We decided not to look at statistical relationships between nitrate and other catchment properties, primarily because the catchment properties that are available to us for this project are generally static or were not developed at a fine enough temporal scale to relate to the variability of the Qratio at each site.

I also suggest the following comments to be addressed in a revised submission:

1. In the second and third paragraph of the introduction section, introduction and study area description are mixed. I suggest moving relevant study area parts (incl. table references) down to the second section. Also, please consider adding a few lines on general climate and physiography of the basin, to draw a more holistic picture of the conditions in the basin for readers unfamiliar with the region early on in the m/s. Later explanatory sentences in the results section may then be shortened/deleted.

We agree and have added a "Study area description" section after the introduction that better describes the basins in our study. Adding this section gave us the opportunity to also explore and explain some of the within-basin variability of basin characteristics (for example precipitation) as compared to the between-basin variability of the same characteristics. We also deleted explanatory sentences about the climate/physiography of the basins that occurred in the results and discussion section.

2. No clear rationale is given why the authors chose one year to describe antecedent flow conditions (p. 11455). Was this decision based on testing conceptual considerations? How does dam storage and the basin size in general influence storage and release cycles?

We address our use of the Qratio previously in this letter. Only in the Missouri River Basin is the magnitude of reservoir storage sufficient to substantially modulate year-to-year streamflow variations (see Table 1 for information on relative storage). The referee's comment is well taken and as a consequence we added some text in the introduction that lists many of the confounding influences that are poorly quantified in large basins: "Exploring hydrologic processes, such as the influence of antecedent moisture conditions on nitrate export, in large basins (defined in our study as > 30,000 square kilometers (km^2)) is complicated by their diverse mix of land cover, topography, geology and climate, in addition to confounding influences of dams, irrigation, and point and non-point pollution sources." Also, the second paragraph of our Conclusions section makes clear that interpretation of results for the Missouri Basin is complicated by the high degree of reservoir storage (as well as irrigation associated with that storage), "The positive relationship observed in the Missouri River (HERM) during mid-high contemporaneous flow conditions (Fig. 4), indicates relationships between antecedent flow and nitrate anomaly not only vary by contemporaneous flow class and basin size but also regionally. The heterogeneity of the Missouri River Basin coupled with high levels of irrigation and dam storage (Table 1) make interpretation difficult but may indicate lower nitrate supply in this basin following a drought, compared to other study basins."

3. The authors reflect on catchment heterogeneity and its influence on the flushing response in the conclusions (p. 11464, l. 23ff), but there is no further investigation on the spatial origin of runoff under different flow conditions. As an example, one could e.g. hypothesize that under low flow

conditions, stream water actually consists largely of water stored for around a decade in the subsurface, and the previous year has little causal connection on riverine nutrient concentrations.

Good point. We've added some text to the "Relationships at mid-low and low contemporaneous flows" sub-section that discusses groundwater residence times and suggests that relationships observed under different contemporaneous flow conditions are likely influenced by different flow paths. For example, we now state: "…inter-annual variations in climate act as a hydrologic driver that influences the mixing of groundwater with different residence times (but rather stable nitrate concentration) resulting in variations of nitrate concentration and flux in streamwater (Gascuel-Odoux et al., 2010). In this context, the significant relationships during mid-low and low contemporaneous flows suggest the groundwater systems for GRCH and MISS-OUT may be influenced by annual variations in surface conditions or climate."

4. I wonder about point source pollution in these catchments, do the authors have information regarding the relevance of nitrate sources besides those from agricultural practice? In large catchments with considerable human population, these types of sources could have an impact on river concentrations and, moreover, contribute intermittently and have a deteriorating impact on long-term regression models.

Thanks for noting this. We agree that our manuscript needs to address the source of nitrate in streamwater and make the case that agriculture is the primary source of nitrate. To do this we used estimates from the U.S. Geological Survey's SPARROW (SPAtially-Referenced Regression On Watershed attributes) model, available online. This model estimates in-stream water quality in relation to upstream sources and basin and climate characteristics. Our investigation using this tool indicates total nitrogen from population-related sources (6 to 22%, depending on the basin) and atmospheric deposition (15 to 32%) can be substantial, but agriculture (51 to 79%) is the dominant source of total nitrogen for the eight basins in our study. We have added a paragraph to the "Study area description" section that discusses these source-estimates in more detail.