Dear Editor,

We would like to thank you and the two reviewers for your constructive comments on our manuscript. We have revised accordingly and provide a point by point treatment of the comments below. We have already responded to reviewer #2 (published in the interactive discussion) but because some of the final revisions differ after considering the reviewer #3’s comments, we include the replies at the bottom of this response. Our comments are in bulleted format after the issues raised by the reviewers.

Comments from the editor
Associate Editor Decision: Publish subject to minor revisions (Editor review) (19 Jan 2016)
by Dr. Roland Bol
Comments to the Author:

Dear authors,

I would take the opportunity to engage with the comments by 3rd reviewer placed on 17th January to have a final stab at the revision the manuscripts and incorporate where relevant the comments and suggestions made by this reviewer. I myself find several Figures, especially Fig. 2, 3 and 6, very hard to see what is in it. Can these figures be made as large as possible, so I can see the symbols and treatments in it clearer. Even Figure 1 suffers from some of the sub-figures being rather small. The authors should also consider if all Figures are truly needed in the main text or if some more can go to supplementary materials.

- We have reformatted the figures to improve readability and clarity and have moved figure 6 to the supplementary information. We have also added more detailed captions so the figures can be understood independently of the text.

Comments from reviewer #3
Anonymous Referee #1
Received and published: 17 January 2016
General comments
This manuscript examines the geological and land use controls on the concentrations of nutrients in freshwaters in three contrasting study catchments in north-western France. The manuscript draws on a 5-year water quality monitoring data set in both base flow and storm flow conditions, collected between April 1996 and August 2000. The paper is well structured and clearly written, however, I’m concerned whether the overall conclusions as they stand at the moment are sufficiently novel, as the different effect of physical controls and land use on water quality at a catchment scale has been demonstrated in a number of previous studies, including some high frequency longterm monitoring experiments (for example, see papers related to the Irish Agricultural Catchments Program but also many others). I would encourage the authors to clarify the novelty of their work in the introduction and conclusions.

- Thank you for the comments. We have reoriented the abstract, introduction, and discussion to emphasize what we see as the most novel contributions of the paper: the direct and indirect influence of geology on water quality and the selective development of vulnerable land surfaces. We have also tried to provide better context to facilitate easier evaluation of the novelty of our work.
Abstract

1. The authors refer to ‘surface roughness’ however this was not measured in this work and is not clearly defined – can you please clarify in methods how the difference in surface roughness was quantified between the three study catchments?

- We have added the methodology to the text and added a roughness index map to the supplementary information (Fig. S10). The 2m resolution digital elevation model (DEM) was used to estimate the roughness. The mean DEM, the max DEM and the min DEM were calculated for a grid of 10x10m. The roughness index was calculated as below:

\[ R = \frac{\text{Mean}_{\text{DEM}} - \text{Min}_{\text{DEM}}}{\text{Max}_{\text{DEM}} - \text{Min}_{\text{DEM}}} , \quad 0 < R < 1 \]

2. Although transient storage and residence time are mentioned in the abstract, these hydrological parameters are not examined later in the manuscript – perhaps some hydrograph analysis of this data set should be undertaken to support this statement?

- We have clarified the methods in the text. Our discussion of transient storage and residence time are based on hydrograph decomposition using high frequency discharge data. We refer to Kolbe et al 2016 (submitted) for characterization of the residence time distribution over the flow domain including a part of G-01 and GS-01. (Kolbe T., Marçais J., Thomas Z., Abbott B.W., de Dreuzy J.R., Rousseau-Gueutin P., Aquilina L., Labasque, T., Pinay G., 2016. Dominance of local flows and extended transit times in shallow aquifers. Submitted, Journal of Hydrology.)

3. ‘Despite agricultural activity : : : the physical context (geology, topography, and land use)’ – can you please clarify how does landuse differ from agricultural activity mentioned in the same paragraph, or restructure the sentence?

- We have rephrased this sentence as: “The influence of geology and accompanying topographic and geomorphological factors on water quality was both direct and indirect because the distribution of agricultural activity in these catchments is largely a consequence of the geologic and topographic context.”

Methods

Catchment characteristics and experimental design – could the authors please also describe the soil types present in the three study catchments? This could help to inform the discussion of the observed water quality differences and likely soil biogeochemical processes impacting on nutrient availability and processing. Secondly, is it possible to estimate how the intensity of agricultural inputs differs between the three study catchments (ie input of organic and inorganic fertilisers, livestock stocking density etc.) as this may also help to explain the observed differences? Finally, did the authors consider calculating and comparing instantaneous nutrient loads, as well as concentrations?

- The soils are mainly loamy. We have added a soil type map to Figure 1. Soil depth is indicated in the Table 1.
• Average fertilizer application is roughly 200 kgN/ha for the research area and does vary with land use. However, because we do not have any measurements of fertilizer application, we simply use land use as a proxy (since differences in fertilizer use would be captured by this variable).

• We did calculate instantaneous and annual nutrient loads. However, because the catchments vary widely in size and the load data closely followed the concentration data, we ended up using concentrations in the final manuscript, which allow more direct comparison.

Water quality analyses – can the authors clarify how was a discharge event defined? Can you please comment on the analytical precision and accuracy of laboratory analyses?

• Discharge Event definition:
  We have added the method to the text. Water level ($h(t)$) was measured every minute. An hourly running mean ($h_{mean}$) was calculated continuously. For each time $t$, the current trigger level $dh(t)$ was calculated as below

  $$dh(t) = h(t) - h_{mean}$$

  *The beginning of discharge event is defined as below: for $dh > 0.3$ cm the automatic sampler start sampling*

• The analytical precision is as follows:
  DOC : 0.5 mg.L$^{-1}$ (sampling volume of 40 mL minimum)
  N-NO3 : 0.05 mg.L$^{-1}$ (sampling volume of 10 mL minimum)
  P-PO4 : 5 µg.L$^{-1}$ (sampling volume of 10 mL minimum)

Spatial data and statistical analysis – can you please specify how was hedgerow density calculated?

• From field campaign and aerial photography, a shapefile with polylines indicating the length of each edge (branch) of hedgerow network was created. Hedgerow density ($H_d$) was calculated as below

  $$H_d = \frac{\sum_{n=1}^{N} L_n}{Area} \quad [L^{-1}]$$

  *Hedgerow density is expressed on m.ha$^{-1}$ in table 1.*

Please give a web page reference and scale for the geological map used.

• All the maps are available on web pages:
  o Geological maps are from BRGM [http://infoterre.brgm.fr/]
  o All the maps of Zone atelier Armorique :

  Can you please also include a soil map to illustrate the differences in soil types between the study catchments?
Results

3.1 Hydrological and land-use analysis – can you please comment on the land use in the riparian zone between the three study catchments – was this significantly different to explain some of the observed differences?

- Riparian zone areas were calculated for each catchment but there was no significant difference. Moreover, Sabater et al. (2003) highlights that nitrate removal rates were similar for herbaceous and forested sites. The observed differences are related to the difference in nitrate inputs (see question 3.2 in the previous section). (Sabater, S., Butturini A., Clément J.C., Burt T.P., Dowrick D., Hefting M., Maître V., Pinay G., Postolache C., Rzepecki M. and F. Sabater. 2003. Nitrogen removal by riparian buffers under various N loads along a European climatic gradient: patterns and factors of variation. Ecosystems, 6: 20-30)

3.2 Effects of catchment characteristics on water chemistry - can you please present a table with the summary of water quality data for each catchment (determinants of interest, mean value, number of samples) in the supplementary information easy comparison? At the moment, it is difficult to understand the size of the dataset and how it captures the likely temporal variability in water quality.

- A synthetic view of the data set indicating the number of samples, the mean value and the standard deviation has been added as Table S2 in the supplementary material.

Similarly, to facilitate easy overview of the data, I suggest reformatting the Figures S2 and S3 to show discharge, rainfall and determinants of interest for each study catchment in a separate graph on a single page (so 3 graphs in total, one for each catchment). A table showing the factor loading scores on the PCA axes would also be beneficial – either in the main manuscript or in the supplementary material.

- As suggested we improved the presentation of Figures S2 and S3 by adding high frequency discharge measurements and rainfall for GS-01 and S-01. Each catchment is presented in a single page. We added a table in the supplements indicating PCA scores for the 3 principal dimensions (table S3).

Inter-annual solute dynamics – please note line 9 is truncated, should end S-01.

- We have corrected the typo.

Discussion

Sentence “We found that carbon and nutrient dynamics differed..” might be better reworded “We found that carbon and nutrient dynamics differed between the three study catchments both on an event and inter-annual temporal scales..”

- We have revised as suggested.

4.1 Proximate and ultimate controls on water quality
Line 14 “buffering the catchment fluctuations in water chemistry” – can you please discuss what soil biogeochemical processes may be responsible for this buffering with reference to the soil types present in these three study catchments?

- The difference in the weathering processes between granite and schist results in deeper soils in the granitic catchment G-01 (mean depth 80 cm) than in the schist (mean depth 45 cm) (GS-01 and S-01). We observed that soil hydromorphy was highest in the granitic catchment. Moreover, livestock pasturelands are more common on granite than on schist, leading to higher DOC availability (see Fig 7) to sustain heterotrophic denitrification. We rephrased the paragraph (section 4.1) to introduce this point.

Lines 4-5, page 15349 “the interactions between catchment context and human use have resulted in preferential agricultural development of schist catchments, which appear to be more prone to nutrient export”. Can you please clarify why these catchments may be more prone to nutrient export? - most likely due to higher soil nutrient content due to higher input of agricultural fertilisers. Have the authors considered whether point sources, such as rural septic tanks, can also be a source of pollution in these study catchments?

- Schist catchments, present to be more prone to nutrient export because of land use is dominated by corn and wheat of the land use (60%). Nitrate export as well as nitrate inputs are highest.
- There was no point source in these predominantly agricultural catchments. Houses and hamlets have individual septic tanks for sewage treatment.

4.2 Controls on chemistry across scales
Line 22, page 15349 You refer to larger overall fluxes of NO3- but it is not clear from Figs. 3, 6 and 7 how these fluxes were quantified and there is no mention in the methods on how nutrient fluxes were calculated. In the paper, you consistently refer to concentrations, while a flux is the mass of nutrients exported over a given period of time.

- In our paper we present only concentration data but in the discussion we refer to general patterns. We have revised so it is clear we are talking about concentration from our study and fluxes in general.

3.2 Hedgerow density and vegetation effect on soil and shallow groundwater You discuss the role of hedgerow density on NO3- mass balance at a larger scale. Line 3 suggests that soil beneath hedgerows may be relatively dry, you then go on to suggest that there may be enhanced removal or retention of NO3- by hedgerows. These two statements appear contradictory, as denitrification is more effective in anaerobic conditions in wet soils. Can it be that hedgerows are a surrogate for land use type and intensity (ie lower inorganic N fertiliser input), which then leads to lower NO3- losses from these headwater catchments?

- Indeed, soils below hedgerow are relatively dry, but even relatively dry soils in Brittany have ample soil moisture to lead to anoxia. Furthermore, the root system increases the organic matter availability in the vadose zone. We tested this hypothesis by analyzing groundwater stratification below the hedgerow (Thomas et al. in preparation). We highlight that root system increases denitrification capacity by increasing organic carbon...
availability in the shallow groundwater. Also, soil thickness increases around hedgerows with fine particles accumulation (silt and loam) which can increase denitrification capacity (Ref. 2 and Ref. 3).

- Indeed, there is a multifactorial effect such as interception, small inputs, etc. But the ratio between vertical and lateral fluxes may increase groundwater mixtures as the boundaries of the system are larger than the hedge network’s width.


Technical corrections

Fig. 2 – Did you consider discussing and comparing seasonal dynamics in nutrient concentrations? These may explain some of the observed differences between the three study catchments. Highest discharge in S-01 appears to be in the spring – presumably following snow melt?

- We have revised figures 2 and 3 to better show the seasonal dynamics.
- In Brittany snow events are rare and there is no snow melt period.

Fig. 4 - Can you please highlight the significant differences between nutrient concentrations in the three study catchments for easy comparison?

- We have revised the caption and text to emphasize these differences. In the granitic catchment (G-01), DOC concentration is higher than those on schist bedrock (GS-01 and S-01). We assumed that this highest DOC concentration is due to meadows land use on granite. N-NO3 concentration is highest in the most intensive agricultural catchment where cereals and corn are the dominants land use (S-01). P-PO4 is also associated to agricultural land use. P-PO4 pics are observed only during discharge events when N-NO3 concentration. Carbon, nitrogen, and phosphorus dynamics were summarized in Figure 6 for yearly concentrations and in Figure 5 with a synthetic view of the set of data.

Fig. 5 – I found this figure difficult to work out – can you please indicate in which direction are discharge and elevation increasing? Why are elevation and chloride blue? Please note that the scale on axis 3 is obscured by the front edge of the cube. Can you please make the figure caption more explicit so that it explains the observed patterns to the reader, without the need to refer to the main body of the manuscript?

- We modified Figure 5 to indicate axis directions. As shown table S3, Elevation and Chloride were used as supplementary variables indicated blue color. We added this explanation to the caption of Figure 5.
Fig. 8 – As for figure 5, can you please provide a more detailed description of the processes illustrated in this schematic in the figure caption. Why are there two hillslopes 1 and 2?

- We have developed the caption and also better explain this figure in the text.

**Comments from reviewer #2**

Received and published: 2 December 2015

We would like to thank the reviewer for his or her constructive comments and suggestions.

The “proximate and ultimate controls” terms need to be better explained in the introduction. Working hypotheses should be presented using these terms.

- We have rephrased our hypotheses in the introduction specifying the proximate controls (land use and hedgerow density) and ultimate controls (geology and topography).

“Base flow” and discharge event” are the considered hydrological periods in this manuscript. High flow period, apart from flood events should be better characterized.

It would allow to get rid of the ambiguity on the nitrate concentration dynamics in the discussion section. Indeed, it seems that nitrate concentrations do not vary with discharge during base flow and high flow periods; yet, they are diluted during flood event.

The effect of rainfall during these events might be necessary to be taken into account.

- We realize that our description of the sampling design was unclear and have clarified in the text that we are referring rather to high-frequency (collected only during storms) and low-frequency data (collected across the hydrograph including both base and high flow periods). Thank you for bringing this up and we think our revisions resolve this ambiguity.

P. 13 line 11: “nitrate was diluted during high flows”. P.12 line 7 “the lack of significant dilution on NO3 during discharge events”. There seems to be a contradiction between these two sentences.

- Indeed as originally stated it is unclear due to a mistake in the text. We have corrected so P.12 line 7 and P. 13 line 9-11 refer to the significant dilution during high discharge events as shown figure 6.

Since hydrology is a controlling factor of concentration, you should discuss the relationship between Define Â´n surface roughness Âž.

- We have defined surface roughness (see response to referee#1) and added a discussion of its effect on hydrology.

Be consistent in the land use description, e.g. corn in Table 1 and maize in Figure 4

- We have revised to use corn throughout.

Chapter 2.2 : add some information on the population density in the drainage basins.
• We will add a sentence about population density in Brittany.

Table 1: leave only one digit. Delete the elevation difference value which is redundant with the 2 previous lines. Add mean interannual specific discharge of the 3 drainage basins.

• We have revised the table as suggested.

P. 8 lines 8-9 should be inserted P. 7 in 3.1 section.

• We have revised as suggested. Thank you.

Chapter 2.3 : how many samples during baseflow and storm event?

• We have specified that there were 174 samples for base flow (now referred to as low-frequency) and 566 during storm event (high-frequency).

What are the specific discharge sampled during flood event?

• Flood event discharge is indicated in Figure 6.

Chapter 2.4 line 27, are you sure you want to refer to Figure 2a?

• We changed the reference to Fig. 1d. Thanks for catching this.

Chapter 3.1 : only rainfall is discussed. There is a discrepancy between rainfall presented in the Table S1 and values discussed in the text.

• In section 2.1 we indicated the annual precipitation which is about 965 mm. Fig S show monthly precipitation for 20 years period the mean interannual was indicated in the plot (up-right). In the text we indicate the actual precipitation for the studied period. We have added an explanation in the text.

Add a description of inter basin and inter annual specific discharge variability

• We added this description in section 3.1.

in Table 3 Figure 4 : add a, b, c

• Added.

Chapter 3.3 : It might be useful to add Figure S4 in the main manuscript. It provides interesting information on DOC, nitrate and PO4 dynamics during flood events.

• Thanks for this suggestion. We agree that this result is really interesting, we moved it to the manuscript.

Chapter 4.2 : explain DON and DOP sources (line 22)

• We added a description that in Brittany, DOM is largely derived from wetlands and hydromorphic soils of bottomlands (see Lambert et al., 2014-BG, Jeanneau et al., 2015-BGD; Hood et al., 2005-BG).

Figure 7: increase the font size for axes and caption

• Changed.
Figure 8: should be better discussed.

- We have added a better description of the conceptual model—particularly focusing on the temporal scaling and transport between hydrologic compartments.