<u>Authors responses to Reviewer #1</u>

General comments: The paper fits very well to the multidisciplinary scope of HESS, connecting Hydrology, Ecology and Environmental questions. The data set is very interesting, because it covers more than a year with high temporal resolution and comprises an exceptional year which is predicted to become more frequent with climate change. This makes the results particularly interesting for management and predictions. Particularly the dynamics of both DOC and nitrate and their relationship is important in this context. The conclusions reached are relevant for nitrate management in agricultural catchments: Times of high nutrient load are defined for different hydrogeological sites in particularly varying with BFI. This data set and the approach is new to my knowledge. Over all the structure of the paper is logical and figures and tables are appropriate. The discussion could be improved by picking up the points raised in the introduction and both could be more compact, for the reader to get your main points. I recommend publication after minor revisions. Please find some suggestions in the specific comments.

We thank the reviewer for their positive comments in relation to scope, interest and relevance for management and future predictions in relation to climate change. Below we indicate the changes that we can make to address the reviewer's recommendations for improvements.

Abstract:

Overall the abstract gives a good summary of the main findings, but the first and the last sentence could be improved:
bullet L 22- L 26: This sentence is very long and confusing, so I would suggest breaking it into two. It is also unclear to me what role climate change (hydrology or DOC, nitrate production?) plays in this sentence. I suspect you refer to the reference of Whitehead et al., 2006 in the introduction. However, without the whole context this sentence is very confusing, as DOC and specially nitrate production and delivery arise from a variety of human impacts, whereas the impact of climate change on hydrology is well known to the reader when starting with the abstract.

We can amend the sentence to as follows to address the reviewer's comments:

'The role that hydrology plays in governing the interactions between dissolved organic carbon (DOC) and nitrogen in rivers draining lowland, agricultural landscapes is currently poorly understood. In light of the potential changes to the production and delivery of DOC and nitrate to rivers arising from climate change and land use management, there is a pressing need to improve our understanding of hydrological controls on DOC and nitrate dynamics in such catchments.'

bullet L 42: The last sentence seems a bit disconnected here from the rest of the abstract, as suddenly DOC stands alone here. How about something like: Consequently, our study emphasizes the tight relationship between DOC availability and nitrate uptake in agricultural catchment and further reveals that this relationship is controlled to a great extent by the hydrological setting. Even though I agree with the authors that research from other catchments would be interesting to extrapolate the findings on a larger scale, I think that over all this is mentioned a bit too much throughout the paper e.g. what future work should do. I would appreciate a reduction of these sentences in the discussion too.

We can remove the final sentence of the abstract and replace with the following text:

'Consequently, our study emphasizes the tight relationship between DOC and nitrate availability in agricultural catchments, and further reveals that this relationship is controlled to a great extent by the hydrological setting.'

Introduction:

bullet The paragraph 4 might be better integrated in paragraph 5, as it includes already predictions and goals (L 135-L 139). Therefore you might consider shifting this section to L 160. This way you would go from the DOC:nitrate removal, land use and climate change in L 125 from paragraph 3, directly to paragraph 5 starting with "Controls of riverine DOC and nitrate arise from: : :". After presenting these controls you could start explaining the specific situation of your study area and what you expect with BFI.

We agree with the reviewer and can remove paragraph 4 from the introduction. We could adjust our research objective (i) to include a description of the contrasting geology that we are considering:

(i)   To quantify the relationship between nitrate, DOC and DOC:nitrate molar ratio with Baseflow Index for six sub-catchments of contrasting geology (Chalk, Greensand and clay) in the Hampshire Avon.

bullet L154-159: very long sentence, maybe a break at L 156: ": : :a wide range of BFI. We hypothesise: : :"

Agreed – we can make the suggested change.

Methods:

Methods: The methods are already very detailed; only the statistical part could be a bit more detailed. The linear mixed effect model approach seems appropriate to me. I just have a question, also concerning the way you report your results later: Could you please explain why you use two different R packages and different significance levels, as well as a different way of reporting them in your results? Chi2, F, r, r2,: : :

We use the lmer function in package lme4 for the surface water data, and the lme function in package nlme for the porewater data because the latter offered us the opportunity to compare mean nitrate and DOC porewater values between sites, whilst the former offered more flexibility with the mixed effect modelling. The two packages provide different statistical outputs. Bates et al (2015) provides a full description of the differences between the two packages. [Bates et al (2015) Journal of Statistical Software, doi 10.18637/jss.v067.i01].

Results:

Comprises of four subsections, which cover (1) Hydrological conditions, (2) BFI and nutrients, (3) BFI and (4) Seasonality: The titles of (2) and (3) could be a bit more specific. For example (2) "Quantification of the relationship between nutrients and BFI" and (3) "Intra-annual variations of groundwater and quickflow contribution"

We can change the titles to those kindly suggested by the reviewer.

bullet L 384 and L 386: Why are these results reported differently?

See comments above.

bullet L 467: It might be helpful to the reader to explain what your definition of old and

new water is already at this point, even it is explained later in the discussion.

We have can add definitions to this text.

Discussion:

The discussion would benefit from the comparison with studies from other watersheds on DOC:nitrate molar ratios and hydrological responses, even if they are from other climate regions (maybe ones which are already characterized by hot and dry summers and wet winters) or less agricultural areas (these are just some examples, but there are many others:

Lupon, Anna, et al. "Contribution of pulses of soil nitrogen mineralization and nitrification to soil nitrogen availability in three Mediterranean forests." European Journal of Soil Science 67.3 (2016): 303-313

Sebestyen, Stephen D., Elizabeth W. Boyer, and James B. Shanley. "Responses of stream nitrate and DOC loadings to hydrological forcing and climate change in an upland forest of the northeastern United States." Journal of Geophysical Research: Biogeosciences 114.G2 (2009);

Andrea, Butturini, et al. "Cross-site comparison of variability of DOC and nitrate c–q hysteresis during the autumn–winter period in three Mediterranean headwater streams: a synthetic approach." Biogeochemistry 77.3 (2006): 327-349.

Tiemeyer, B.,and P. Kahle. "Nitrogen and dissolved organic carbon (DOC) losses from an artificially drained grassland on organic soils." Biogeosciences 11.15 (2014): 4123.).

We thank the reviewer for providing details of additional references to include in the paper. We do compare the results of our study with those obtained for multiple land use types across the USA, reported in the US LINX II study, but agree that more can be made of comparisons with other regions and land use types (although note that Lupon et al reference above does not provide DOC data to accompany the N data).
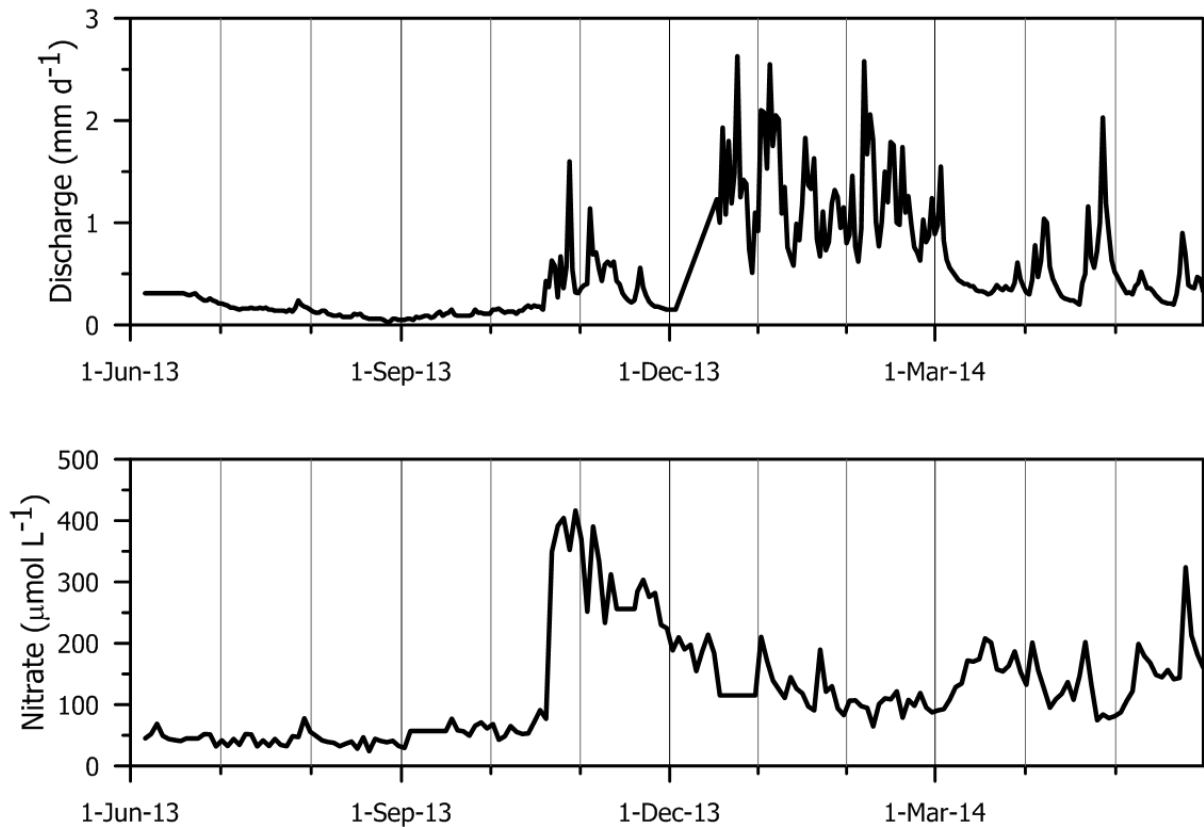
L 496: Maybe you could introduce an abbreviation for EC and Q in the beginning and use it all the text, since both are used many times

We find the use of too many abbreviations potentially confusing so would prefer to keep the text as is. In this case we have avoided using EC in particular due to potential confusion with our site CE.

Section 4.3.: Here it would be useful if you could go back and pick up the points from your introduction, where you cite Whitehead et al., 2006 and Jiang et al., 2010 etc.: In the sense of does your study goes in line with their predictions and concerns?

We could address this suggestion as follows:

Provided supplementary information (Figure S1) with a time series of discharge and nitrate for site AS to show the flushing of nitrate into the river during Autumn.

Discharge (mm d^{-1})

3
2
1
0

1-Jun-13   1-Sep-13   1-Dec-13   1-Mar-14

Nitrate (µmol L^{-1})

500
400
300
200
100
0

1-Jun-13   1-Sep-13   1-Dec-13   1-Mar-14

Add the following text to the manuscript:

'The elevated concentrations of nitrate observed in the River Sem in Autumn 2013 , provide some additional evidence to support results from dynamic modelling using INCA-N which show that drought conditions followed by wetting up of soil (as predicted in future climate change scenarios) can give rise to high nitrate loads in rivers (Whitehead et al., 2006). However, we observed this flushing effect most markedly in the clay sub-catchment of the Hampshire Avon where the majority of nitrate is likely to be delivered to the stream through shallow subsurface pathways, as opposed to the Chalk catchments where groundwater contributions of nitrate dominate.'

L 581: could arise from mineralisation? Please explain how exactly the DOC concentration can increase due to mineralisation. I could not find anything about this in Aubert et al., 2013 and to my knowledge mineralisation is a process that rather reduces DOC concentrations.

Yes rather than mineralisation we mean production of DOC. We apologise for the error. Aubert et al note the production of DOC follows inter-annual patterns controlled by surface biological processes influenced by temperature. We can alter the text accordingly.

L 662: A citation would be useful here to back up your statement

We propose to add Rodriguez-Cardona et al (2015) here to support the statement.

L 677-682: This sentence is very long. Please make a point before and also suggests in L 679. In the second sentence you could say specifically winter, this way your conclusion becomes clearer.

Many thanks for the suggestion. We can amend the text as follows:

'Our research gives added impetus to the need to control autumn run-off from drained, grassland catchments supporting intensive livestock farming. Our study also suggests that during winter, periods of lateral flow and over-bank flooding in areas of intermediate BFI, such as Greensand, may export a significant proportion of the annual nitrate load with little opportunity for in-stream nitrate processing or removal.'

Conclusions:

The conclusions could be a bit more to the point, meaning it is hard to understand from the conclusions, what are the main achievements of this study. Overall, I am wondering if the conclusions are really necessary, subsection 4.4. gives already a good idea on what the main findings and their implications are. If you keep the conclusions, I would suggest shorting them to one paragraph.

For example, L 688- L 690 is already explained in the discussion. Also L 707- L 711 could go out.

We would like to keep the conclusion to highlight the main achievements of the study but we can shorten these to bullet points as suggested by the reviewer.

L 714- L719: This sentence could be shorten: In this way, the spatial arrangement of areas of contrasting BFI within a catchment may have important ecological and biogeochemical consequences for receiving waters, especially if they are designated as NVZ or transitional and near-coastal areas.

We can shorten the sentence following your helpful suggestion.

Tables and Figures: In general tables and figures are clear and accompany well the text. I would suggest writing DOC instead of Dissolved Organic Carbon at the figure axes.

We can use DOC instead of Dissolved Organic Carbon for Figure axes.