

## ***Interactive comment on “Hydrological controls on DOC : nitrate resource stoichiometry in a lowland, agricultural catchment, southern UK” by Catherine M. Heppell et al.***

### **Anonymous Referee #1**

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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

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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.

## Specific comments:

Title: The title is appropriate

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.

*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.

Introduction: The introduction comprises of 5 paragraphs, which cover (1) the need to study nitrate and the problem of managing nitrate in rivers, (2) the role of DOC in stream ecological processes, (3) the interplay of these two nutrients, (4) the specific situation in the UK and the predicted relationship with BFI and finally (5) the

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hydrological controls on DOC:nitrate ratios.

*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.

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

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? Chi<sup>2</sup>, F, r, r<sup>2</sup>, . . .

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”

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

*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.

Discussion: The discussion has four subsections which do not follow the exactly same pattern as the goals stated in the introduction and continued in the results section. However, the order and the separation of the topics into the subsections, starting with hydrological aspects (1), continuing with BFI (2), then seasonality (3) and closing with environmental implications of this study (4) also seems logical to me. 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.).

*bullet* 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

*bullet* 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?

*bullet* 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.

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

*bullet* 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. 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

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

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.

Technical comments: *bullet* L 30, 31, 32 and 36: Baseflow Index is already defined as BFI in L 28

*bullet* L 48: suggest to introduce abbreviation nitrogen (N) at this point

*bullet* L 137: suggest to introduce abbreviation Baseflow Index (BFI) at this point

*bullet* L 145: shouldn't the power function written like that with a small "a":  $C = aQ^b$  ?

*bullet* As suggested already in the introduction: Baseflow Index -> BFI, capital letters or small? L 195 and L 196

*bullet* L 206: you always wrote c., here you write circa

*bullet* L 223: Temperature is written twice

*bullet* L 266: Citation correct?

*bullet* L304: Baseflow Index -> BFI

*bullet* L328: Baseflow Index -> BFI

*bullet* L 348: SMD already defined in Methods

*bullet* L 371: round all  $\chi^2$  to 2 digits

*bullet* L 388: There is a ) missing.

*bullet* L 399: Citation Field, 2000 is 2002 in bibliography.

*bullet* L 408: baseflow indices -> BFIs

*bullet* L 469: occurs -> occur

*bullet* L 475 and 479: just spring, without the?

*bullet* L 599: Above the (instead of our) threshold. . .

*bullet* L 650: greensand and chalk is written with capital letters throughout the paper.

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Why different here?

*bullet* L 670: electrical conductivity (small letters)

*bullet* L 718: abbreviation NVZ already defined in discussion

*bullet* Figure 3: Suggest putting  $r^2$  and  $p$  in all figures, not necessary to write baseflow index everywhere, as it was already defined as BFI.

*bullet* Figure 5: Caption: in the text you write discharge and electrical conductivity always with small letters.

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