Hydrol. Earth Syst. Sci. Discuss.,
https://doi.org/10.5194/hess-2017-30-AC2, 2017

Hydrology and Earth System Sciences
Discussions

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

Catherine M. Heppell et al.

c.m.heppell@qmul.ac.uk

Received and published: 18 June 2017

Authors responses to Reviewer #2

This is an interesting and well-written paper that will be of interest for many in the hydrological community. The research questions investigated are relevant for managers of lowland agricultural catchments and the focus on DOC:Nitrate ratios is novel. The overall quality of the research is high, although occasionally there is a tendency to drift towards speculation (e.g. with reference to the different flowpaths operating in the catchments) without presenting all the necessary data to support these statements. There are two key drawbacks to the paper at present that require addressing. The first is that nutrient samples were collected at 48 h intervals, which means that many short-term storm events may potentially have been missed and thus nutrient loads underestimated. As no discharge time series are presented, it is not possible to say whether this is the case. The authors should recognise this explicitly in the text.

We propose to add a time series of discharge and nitrate as supplementary material. This will also help to address comments of Reviewer 1 in relation to autumn first flushing of nitrate. This will enable us to explicitly state that nutrient loads may be under-estimated due to frequency of monitoring (although note that we do not present absolute loads in this paper, but focus instead on proportional loads by season).

Secondly, the authors discuss at length how changes in C:N stoichiometry may limit the potential for in-stream uptake of inorganic nitrogen, but give far less attention to the equally important role of hydrological residence times in influencing these processes (e.g. Zarnetske et al, 2012, WRR). A better discussion of how these respective reaction and transportation factors interact to influence reach-scale nutrient transformation rates may be warranted here, particularly given the apparent importance of high discharge (and therefore velocity) periods for nutrient mobilisation and export.

The interplay between residence time and reaction rates in the hyporheic zone are the focus of another publication arising from this research in which we explicitly measure residence time and compare to reaction rate (but under baseflow conditions only). We would prefer to keep the focus here on the interactions between DOC and nitrate that were observed in the river and riparian porewater, because we do not quantify either reaction or transport here (i.e. we did not directly measure residence time or denitrification in the wider catchment so we can only speculate that autumn flushing of nitrate occurs in part due to reduced residence time in soils as water flows from the soil surface through macropores and artificial drains).

Abstract:

L39: ‘Storm events’ is perhaps somewhat misplaced in this context. Many readers will interpret this phrase as meaning short-term (hours) intense rainfall events that result in rapid changes in streamflow and biogeochemical dynamics. Yet the frequency of sampling in this study (48 h) is not sufficient to capture this variability. I suggest recasting this sentence (and similar others throughout the text) to clarify that 'storm events' relates more generally to the wetter conditions experienced during autumn and winter months.

The relationship between Q and nitrate and/or DOC concentration during the winter period does capture the influence of storm events, but we also appreciate that sampling of finer, temporal resolution would also be beneficial to fully characterise storm events. We agree that in the abstract the emphasis should be on the winter and autumn periods rather than storm events per se, so we can amend the abstract by removing reference to storm events when describing responses of sub-catchments as follows: '(e.g. winter in sub-catchments underlain by Chalk and Greensand, and autumn in drained, clay sub-catchments)'

Introduction: L92: I agree with the authors that more research into DOC dynamics in lowland agricultural streams is important.

Thank you for the positive comment. We also feel that this area is currently under-researched, and yet potentially extremely important for nutrient cycling in such catchments.

The Introduction as a whole is rather long and could be shortened considerably. As it stands, the key arguments do not stand out clearly.

L127 and 139: It would be useful to state in this paragraph that baseflow index indicates the groundwater contribution to streamflow. Also, the authors should provide more justification for their prediction regarding the link between BFI and NO3.

We can remove this paragraph (following recommendation of Reviewer 1) to help shorten the introduction. We can also amend a later sentence to clarify that baseflow index indicates the groundwater contribution to streamflow (see line 143-144).

'We might hypothesise that groundwater dominated areas (characterised by a high Baseflow Index)....'

L141: This sentence seems repetitive of the start of the previous paragraph.

We hope that by removing the previous paragraph we have addressed this redundancy.

L176: The start of Objective 3 seems repetitive of Objective 1.

We can shorten objective 3 to read as follows:

'To assess the potential implications of any spatio-temporal variations in DOC:nitrate ratios for future nitrogen management.' Methods:

L225: Was the Manta 2 cleaned at any point during the study period? If so, at what frequency? Did this affect the results and if so, was a correction applied?

Yes, all probes on the Manta were cleaned every two weeks, and a manual dip taken in the stilling well for calibration of the water level sensor. A correction was applied to the water level data when necessary on the fortnightly basis. The electrical conductivity probe was calibrated once a month. No drift in electrical conductivity was observable during the study.

L228: Can the authors confirm no sample degradation occurred in the time between collection and analysis? Two weeks is a long time for samples to sit in an unpreserved state.

We carried out laboratory experiments at the beginning of the project to check for evidence of sample degradation over the timescale of one month and did not find any significant sample degradation for nitrate and DOC over two weeks. In addition, at the time of each sample collection, a standard sample was left in the field (in the autosampler box) for the following 2 weeks to check for changes in solute concentration so that any necessary corrections could be applied. In practice this did not prove necessary for nitrate or DOC.

L303: When comparing 48 hr nutrient samples with 15 min Q values, were instantaneous Q values at time of nutrient sampling used? Or were these integrated over longer time period?

Water samples were collected at 09:00 GMT every 2 days, so the corresponding Q value at 09:00 GMT on the same day of sample collection was used (i.e. instantaneous Q values at the time of nutrient sampling).

L381 and 465: Care is needed here to avoid placing text in the Results that would be better suited to the Discussion.

We feel that these sentences are largely descriptive observations and do not stray into the territory of a discussion so we would propose to leave these as they are.

Discussion:

L445: Are these trends descriptive only or can they be quantified?

We feel that the trends here are evident on the graph and do not require further quantification. We could calculate a slope for the first trend and a seasonal average for the second, but these would be site-specific.

L462: A discharge time series would be nice to prove that 'autumn storms of intermediate discharge' are really storm events (as mentioned earlier) and not just seasonal shifts in baseflow.

Many thanks for the useful comments in relation to storm events vs seasonal shifts in baseflow. In earlier drafts of the manuscript we considered including a time series but decided to keep the number of Figures manageable. In this revised version, following your recommendation, we offer supplementary material (Figure S2) that illustrates a time series for rainfall, electrical conductivity and discharge for the clay site, AS. We hope that this will address your comment above and also your request to show the

Printer-friendly version

Discussion paper

rapid response of electrical conductivity to rainfall to support the discussion later in the paper.

Throughout the Results section there are references to different years (e.g. L462) but this is not evident in the figures.

The Figure captions state the year of data collection (June 2013-2014 for the nitrate and DOC datasets).This information was missing from Figure 7 so we can add the dates.

L556: Some discussion of other land use types in the catchment and their potential influence on DOC would be useful here. Also, what potential is there for instream production?

The research took place in headwater catchments all selected for their rural characteristics (i.e. without significant contributions from urban land use) and without significant contributions from woodland. Major land use types (arable and grassland) in each catchment are summarised in Table 1 and we can add a statement as to the potential role of grassland in contributing DOC here. Elevated concentrations of DOC were observed in Spring and could potentially be due to in-stream production – this is explained in Line 580.

L612: Given that the discussion focuses heavily on flow pathways within the catchment, it would be helpful to show the rapid response of EC to rainfall events to support this statement.

Many thanks for this helpful suggestion. We have provided supplementary material (see Figure S2) with an example storm hydrograph to show the rapid response of EC to rainfall.

L664: This text could be expanded a little to place the results of this study in a wider context and make comparisons with previous research in this field.

Reviewer 1 also requested that the text be expanded in relation to references provided

Printer-friendly version

Discussion paper

in the Introduction and so we have suggested a way forward in our response to Reviewer 1. We agree that we can expand the text to make comparisons with previous research in this field.

Technical corrections:

L127: Not just the UK. L135: Provide indicative range.

This text will be removed following recommendation of Reviewer 1.

L145: Define meaning of letters in equation.

Definition of letters can be included in the text.

L154-160: Suggest splitting this very long sentence. Will do.

L171: Clarify whether three or six sub-catchments are involved in the study.

Six sub-catchments are included for the comparison with BFI and then a sub-set of three are used to illustrate seasonal trends.

L195: Ref to support this?

Geology is covered by Bristow et al 1999 reference above.

L215: Provide number of points and R2 value for stage-Q relationship.

C. 14 points were used for each site for the stage-Q relationship with $r2 > 0.96$

L266: How often were samples retrieved?

Samples were collected weekly. We will amend the text to state this.

L281: Provide precision and LOD information for autoanalyser and TOC-L.

For the inorganic nutrient analyses, and for DOC, we required an RSD of < 2%. Limits of detection for the analyses were 0.01 mg N/l NO3-N and 0.03 mg C/l DOC.

L291: Check reference date.

Should be corrected to 1992 in the text - thank you for pointing this out.

L327: Provide indicative number of samples for those included in the analysis.

Number of samples ranged from 12 to 56 depending on the site. Text can be added to state this.

L368: State type of correlation analysis used (Pearson or Spearman)

Pearson correlation analysis was used to explore relationships between solutes (nitrate and DOC) and BFI. We can add a statement in the data analysis section (3.2) to explain this.

L510: Does "the data" refer to EC-Q relationships?

Yes – we can clarify this in the text.

L571: Need to clarify here that the absolute concentration will change but the flow-weighted concentration won't (see Basu et al 2010 GRL)

Here we mean that the absolute concentration of geogenic solutes is maintained at higher discharge due to supply from the groundwater. We have not assessed flow-weighted concentration as we do not use data from multiple years as in Basu et al (2010); instead, we use the definition of chemostatic used in Godsey et al (2009). We can alter the text to clarify this as follows:

'The Chalk site (CE) is near-chemostatic with respect to total dissolved solutes and nitrate. This means that the concentration of geogenic solutes and nitrate is maintained at higher discharge, so that discharge drives solute load and hence the export of solutes to the coast. Here, we use the definition of near-chemostatic expressed in Godsey et al. (2009) as a slope of close to zero on a log(C)-log(Q) plot where C is concentration and Q is discharge.'

L573: By whom? Citation needed.

We will add Basu et al (2010) here.

Fig 1: Sites AS and GN seem in the same place. Also, can differences in baseflow indices be indicated.

AS and GN are very close together. They are at the confluence of two tributaries and the rivers run either side of the same field at this location so it is difficult to show the difference on a map of this scale. Baseflow index is summarised in Table 1 and we would prefer not to over-clutter the map with too much information.

Please also note the supplement to this comment:
http://www.hydrol-earth-syst-sci-discuss.net/hess-2017-30/hess-2017-30-AC2-supplement.pdf

---

Interactive comment on Hydrol. Earth Syst. Sci. Discuss., https://doi.org/10.5194/hess-2017-30, 2017.

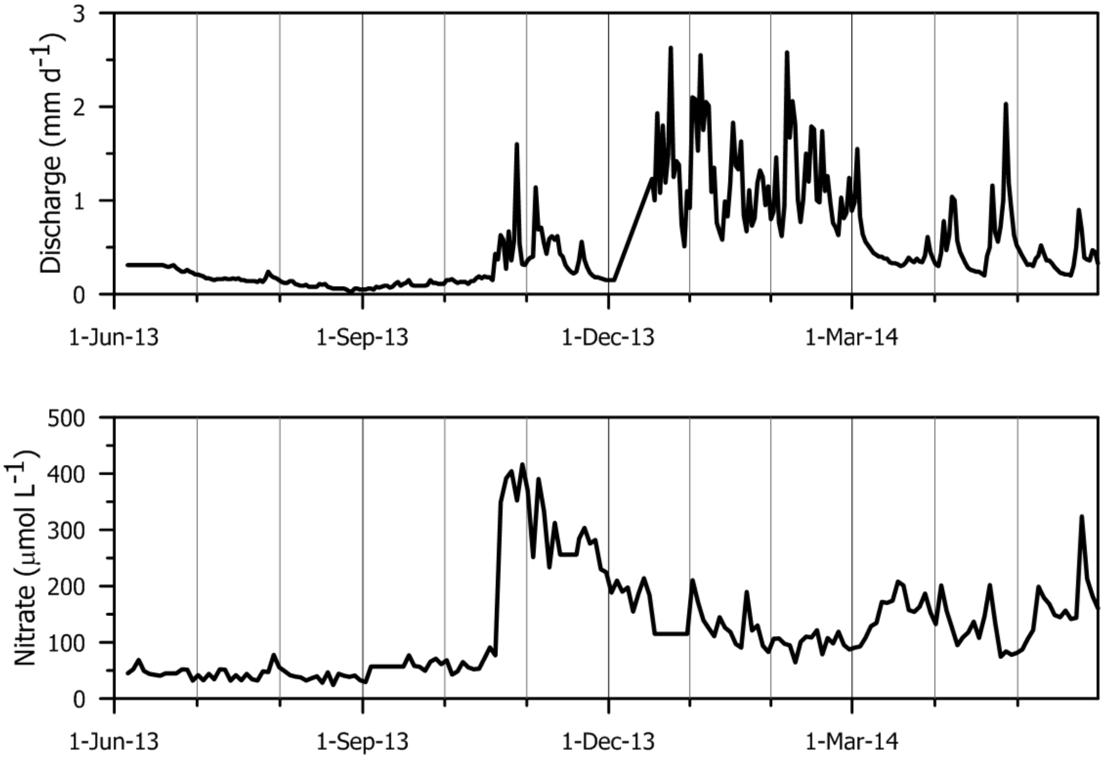

Fig. 1.

Printer-friendly version

Discussion paper

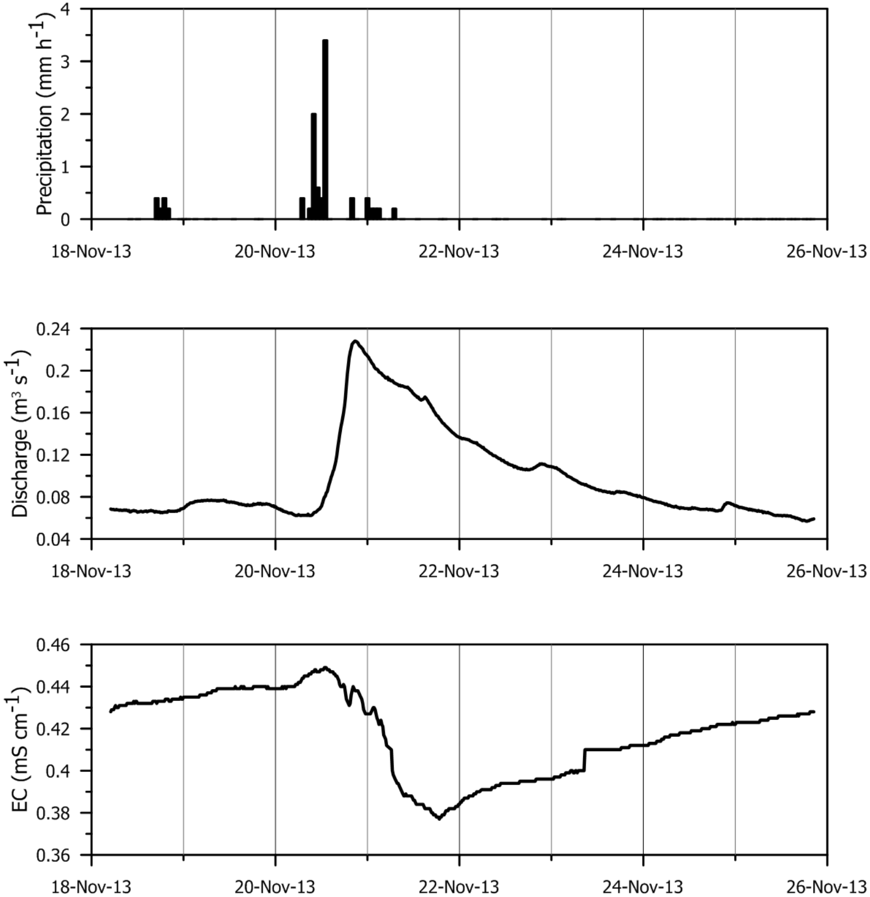
Precipitation (mm h-1)
4
3
2
1
0
18-Nov-13
20-Nov-13
22-Nov-13
24-Nov-13
26-Nov-13
Discharge (m3 s-1)
0.24
0.2
0.16
0.12
0.08
0.04
18-Nov-13
20-Nov-13
22-Nov-13
24-Nov-13
26-Nov-13
EC (mS cm-1)
0.46
0.44
0.42
0.4
0.38
0.36
18-Nov-13
20-Nov-13
22-Nov-13
24-Nov-13
26-Nov-13

Fig. 2.