Dear Editor,

Many thanks for your positive comments on our manuscript. Below we have appended our responses to the reviewers, and a manuscript with the changes to address their comments marked in red. We hope that this satisfactorily addresses the required revisions.

Kind regards,

Kate Heppell

Authors responses to Reviewer #1

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).

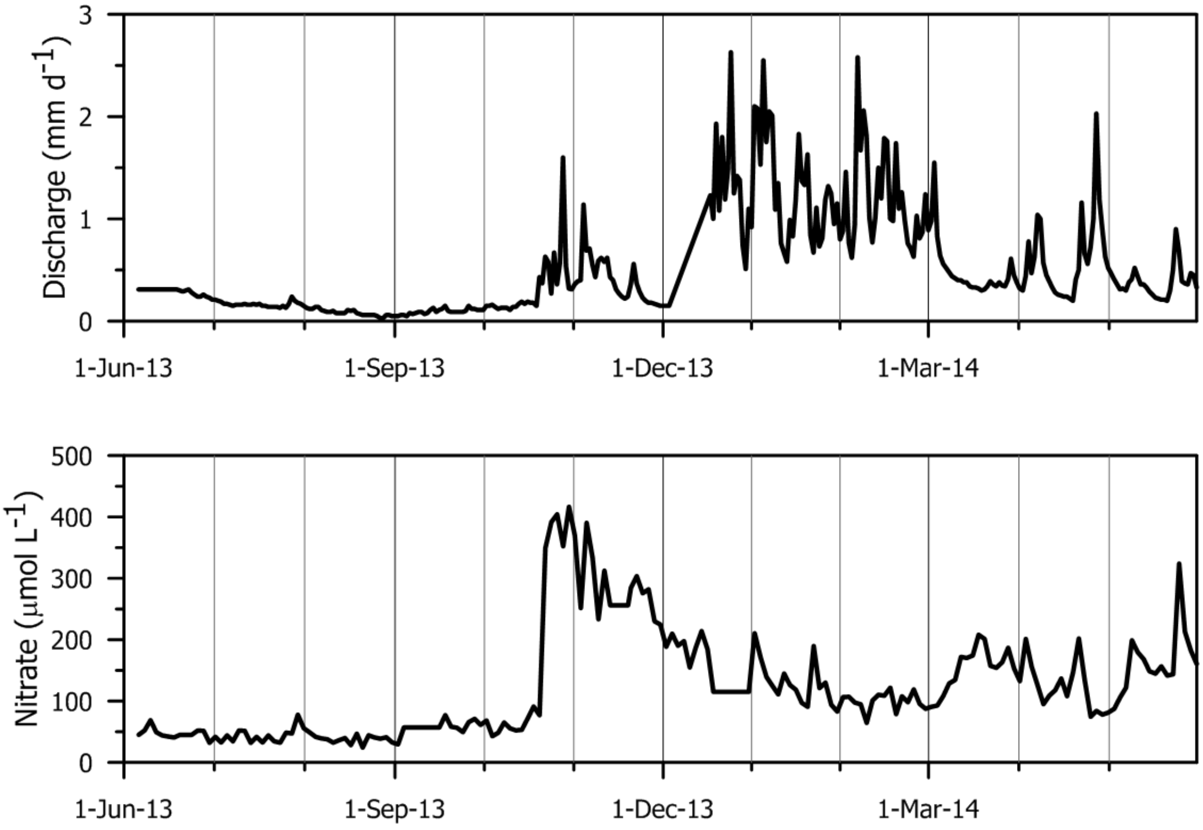
L 496: Maybe you could introduce an abbreviation for EC and Q in the beginning and use it all the text, since both are used many times

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.



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.

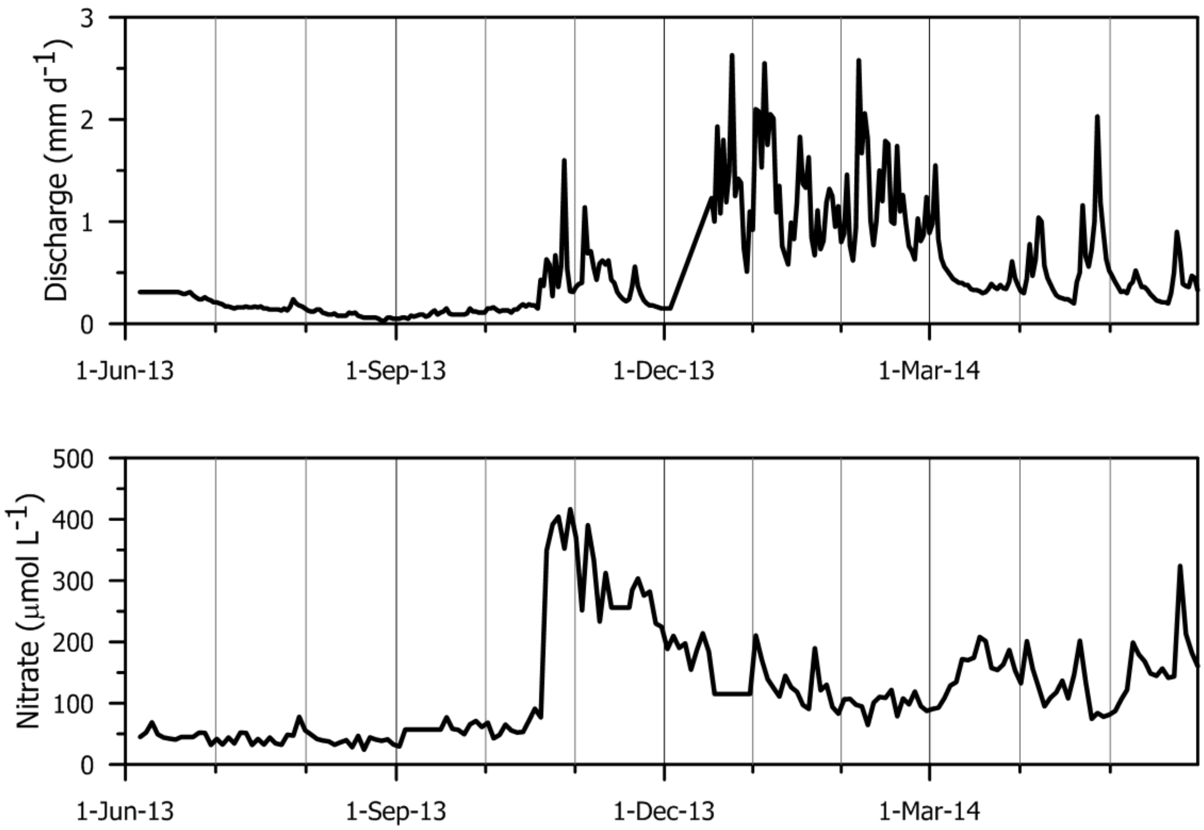
Tables and Figures: In general tables and figures are clear and accompany well the text. I would suggest writing DOC instead of Dissolved Organic Carbon at the figure axes.

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

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.

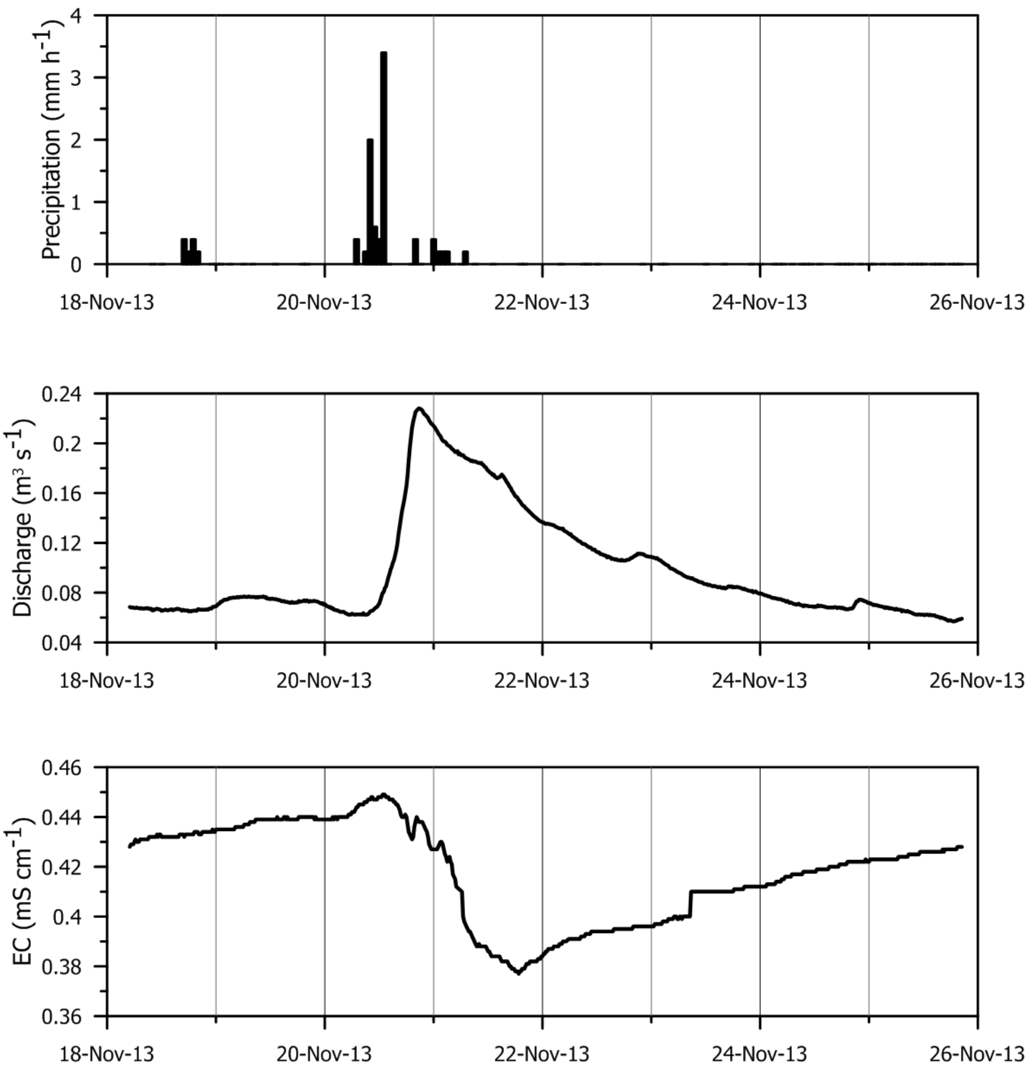
Discussion:

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 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 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 $r^2 > 0.96$

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 NO_3-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.

Hydrological controls on DOC:nitrate resource stoichiometry in a lowland, agricultural catchment, southern UK.

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Abstract

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. We measured DOC and nitrate concentrations in river water of six reaches of the lowland River Hampshire Avon (Wiltshire, southern UK) in order to quantify the relationship between BFI (BFI) and DOC:nitrate molar ratios across contrasting geologies (Chalk, Greensand and clay). We found a significant positive relationship between nitrate and BFI ($p<0.0001$), and a significant negative relationship between DOC and BFI ($p<0.0001$), resulting in a non-linear negative correlation between DOC:nitrate molar ratio and BFI. In the Hampshire Avon, headwater reaches which are underlain by clay and characterised by a more flashy hydrological regime are associated with DOC:nitrate ratios > 5 throughout the year, whilst groundwater-dominated reaches underlain by Chalk, with a high BFI have DOC:nitrate ratios in surface waters that are an order of magnitude lower (< 0.5). Our analysis also reveals significant seasonal variations in DOC:nitrate transport and highlights critical periods of nitrate export (e.g. winter in sub-catchments underlain by Chalk and Greensand, and autumn in drained, clay sub-catchments) when DOC:nitrate molar ratios are low, suggesting low potential for in-stream uptake of inorganic forms of nitrogen. 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.

1 Introduction

As we enter the Anthropocene, the increase in nitrogen (N) concentrations in the natural environment, arising from the combined effects of agricultural intensification and fossil fuel use, is causing pressing environmental problems (Vitousek et al., 1997; Carpenter et al., 1998; Galloway and Cowling, 2002; Rabalais, 2002). An increase in concentrations and loads of nitrate in freshwater environments is one such issue arising from diffuse agricultural pollution, often correlated with the eutrophication of coastal areas (Billen et al., 2011; Houses of Parliament, 2014; Howarth et al., 2012; Vitousek et al., 2009; Withers et al., 2014). Furthermore, in permeable geologies, responses to land management initiatives targeted at reducing nitrate loading are delayed due to long water residence times, with little effect seen in some groundwater-fed catchments over decadal timescales (Howden et al., 2011; Tesoriero et al., 2013; Wang et al., 2012; Wang et al., 2013; Wang et al., 2016). In the United States, a legacy of accumulated nitrate in heavily managed, agricultural catchments has been associated with temporal invariance of annual flow-weighted concentration (a biogeochemical export regime termed chemostatic) irrespective of the permeability of the geology and soil type (Basu et al., 2010). These managed catchments are considered to be transport limited with regards to nitrate; meaning that solute export is controlled predominantly by hydrology rather than biogeochemistry (Basu et al., 2011). Thus changing climate, with important, potential implications for rainfall patterns and hydrochemical responses in rivers, is adding a new urgency to understanding and managing the issue of excess nitrate in our agricultural-dominated landscapes (Howarth et al., 2011). In the UK, there is concern that warmer, drier summers and wetter winters may lead to increased nitrate export from lowland catchments (Whitehead et al., 2009), one scenario being an increased accumulation of nitrate in soils by mineralisation in hot, dry summers followed by flushing of nitrate from soils during autumn at the end of the drought (Whitehead et al., 2006) especially in conjunction with first-flush responses (Jiang et al., 2010; Yang et al., 2015; Orr et al., 2016). However, considerable uncertainty exists around current predictions (Heathwaite, 2010); and policymakers lack results from studies at appropriate temporal and spatial scales for confident decision-making (Watts et al., 2015).

Over the last decade, there has also been an increasing awareness of the significance of the transport and transformation of carbon in fluvial systems within the overall conceptualisation of the global carbon cycle; and freshwaters are now recognised as critical contributors to global carbon fluxes (Dagg et al., 2004; Beusen et al., 2005; Battin et al., 2009). In addition, there is an increased understanding that establishing the factors that control water-borne carbon fluxes is key to predicting the likely implications of climate change for patterns and magnitude of organic carbon transport through freshwaters (Aitkenhead and McDowell, 2000). Although dissolved organic carbon (DOC) plays a crucial role in stream ecology (influencing processes such as nutrient uptake and the balance between heterotrophy and autotrophy) our understanding of terrestrial-to-aquatic transfers, aquatic processing of DOC and its character in lowland, agricultural streams is incomplete (Stanley et al., 2012; Yates et al., 2016, Aubert et al, 2013) as much of the effort in this area has been focused on forested catchments, boreal peatlands and/or upland landscapes with significant wetland cover (Frost et al., 2006; Ågren et al., 2007).

Macronutrients are not cycled in isolation, and important ecological consequences arise from their interplay (Dodds et al., 2004); a key focus of current research is on the linkage between essential nutrients such as carbon (C) and nitrogen (N). Although these elements exist in many forms in river systems, the most abundant biologically-available form of the compounds in lowland, intensively farmed catchments are likely to be DOC and nitrate (Taylor and Townsend, 2010) with nitrate typically contributing > 70% of the total dissolved N species (Durand et al., 2011). The speciation of N in lowland agricultural catchments in Europe has been reported previously (see Durand et al (2011), including in one of the sub-catchments (River Wylye) that is a component of this study (Yates and Johnes, 2013; Yates et al., 2016), but without comparison to the simultaneous behaviour of DOC. This paper therefore focuses on both nitrate and DOC, as the availability of DOC in a stream ecosystem may influence both the quantity and speciation of N exported downstream (Goodale et al., 2005; Bernhardt and Likens, 2002; Grebliunas and Perry, 2016). Taylor and Townsend (2010) synthesised global datasets for DOC:nitrate ratios from groundwater to the open ocean, and hypothesised that an observed threshold ratio of around four was indicative of the shift in carbon to N limitation in rivers representative of the stoichiometric demands of microbial anabolism. Taylor and Townsend (2010) suggested that, at low DOC:nitrate ratios, the extent of nitrate accrual in global waters may be restricted by the rapid conversion of nitrate to nitrogen (N_2) gas via denitrification, whereas at high DOC:nitrate ratios heterotrophic N assimilation may strongly reduce in-stream nitrate concentrations. Whole-stream nutrient additions to rivers characterised by varying land use (using the 'Tracer Additions as Spiralling Curve Characterisation' methodology) have provided experimental evidence that DOC:nitrate ratios are strongly positively correlated with the rate of whole stream nitrate removal (see results from Mulholland et al. (2015) presented in Figure 7 of Rodríguez-Cardona et al. (2016)), although such experiments cannot distinguish between nitrate removal via assimilation and/or denitrification mechanisms. In summary, there is a need to understand whether monitoring DOC:nitrate ratios in rivers could prove a useful component of a toolkit for adaptive nitrate management of river catchments in response to, for example land use or climate change.

Controls on riverine DOC and nitrate arise from a combination of terrestrial accumulation, transfer to the river and in-stream transformations (Stanley et al., 2012). The transfer of DOC and nitrate from terrestrial sources to the channel by hydrological mechanisms results in changing relationships between concentration and river discharge, often described by a power function ($C=aQ^b$ where C is concentration and Q is discharge) which can exhibit marked intra-annual dynamics (Oeurng et al., 2011; Morel et al., 2009; Basu et al., 2010; Outram et al., 2014). Therefore, integrated annual measurements risk masking important seasonal patterns in terrestrial-to-aquatic transfers and export of DOC and nitrate, arising from variations in hydrological pathways throughout the year, such as the interplay between groundwater and shallower lateral flows due to wetting up of upper soil horizons in response to autumn rain (Prior and Johnes, 2002; Sandford et al., 2013; Outram et al., 2014; Yates and Johnes, 2013). Such intra-annual variations in solute chemistry have been termed the 'hydrochemical signature' of the catchment (Aubert et al., 2013). This hydrochemical signature is especially important to consider across an agricultural landscape characterised by a wide range of Baseflow Index (BFI). We might hypothesise that groundwater dominated areas (characterised by a high BFI) will exhibit a stable, more damped, hydrochemical response throughout the year, whereas sub-catchments of low BFI might exhibit a wider range of nitrate and DOC concentration arising from varying contributions of rapid hydrological pathways (i.e. quickflow). Thus, here we aim to develop a spatio-temporal understanding of the processes controlling loading of DOC and nitrate to a lowland, agricultural catchment (Hampshire Avon, UK), which is essential for understanding and managing their combined ecological impact. Furthermore, as our study took place during a period of drought and subsequent flooding in the UK, a focus on seasonality may help to identify any critical periods of nutrient export under future climate change scenarios of drier summers and wetter winters.

To summarise, our research objectives were as follows:

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

(iii) To assess the intra-annual variations in contributions of groundwater and quickflow to streamflow across three sub-catchments representing high, intermediate and low Baseflow Index, and; establish the extent to which nitrate and DOC transport in the catchment arises from the interplay between groundwater and quickflow components.

(iv) To assess the potential implications of any spatio-temporal variations in DOC:nitrate ratios for future N management.

2 Materials and methods

2.1 Site description

The research was undertaken at six river reaches in the Hampshire Avon upstream of Salisbury (Wiltshire, UK), representing sub-catchments of contrasting geology (clay, Greensand and Chalk), and a gradient of BFI (Figure 1; Table 1). The majority of the upper catchment of the Hampshire Avon (draining c. 1390 km^2 in total), is dominated by the Cretaceous Chalk geology, and the hydrogeological properties of these geological units are described in detail in Allen et al., (2014). Sites CW on the river Wylye and CE on the river Ebble are river reaches characterised by high baseflow indices (>0.9) where Chalk provides the main source of groundwater (Allen et al., 2014). In the north and west of the Hampshire Avon catchment there are also significant groundwater contributions from geological formations of Upper Greensand which comprise fine-grained glauconitic sands and sandstones (Bristow et al., 1999). The sub-catchments of sites GN on the river Nadder in the west of the catchment, and GA in the north of the catchment, both comprised c. 50 % Upper Greensand by area with BFI of 0.695 and 0.861, respectively. The two sites characterised by the lowest BFI, sites AS (0.372) and AP (0.234), are located in the sub-catchment of the river Sem underlain by impermeable Late Jurassic Kimmeridge Clay (usually a non-aquifer) and thin interbedded limestone from which limited groundwater flow may occur (Allen et al., 2014). Agricultural land use dominates the Hampshire Avon catchment with arable farming including horticulture comprising 42% of land use, and improved grassland for dairy and beef production covering 23% of the catchment (Natural England, 2016). The distribution of arable and livestock farming varies with sub-catchment; improved grassland dominates in the clay catchment of the river Sem (AS and AP), where it supports intensive dairy production, whilst arable agriculture represents c. 50% of land use at the chalk sites (CW and CE), with sheep grazing and intensive pig production as minority land uses (Table 1).

2.2 Field instrumentation

Sites AS, GA, GN and CE were instrumented for two years from June 2013 until June 2015. Stream stage was measured using pressure transducers (HOBO U20-001-01, Onset Corporation, USA at AS, GA and GN; Levelogger Edge, Solinst, Canada at CE) in a perforated stilling well, logging at 15-mins intervals. Regular (fortnightly when possible) manual measurements of discharge by the velocity-area method enabled construction of stage-discharge relationships for each site. Discharge values used in the analysis were scaled to mm day^{-1}, using an assumed catchment area defined by the topographic divide for that point in the stream network. Rainfall was measured at 15-mins intervals at AS, GA and CE using a tipping bucket raingauge (674, Teledyne ISCO,USA) in order to calculate daily rainfall totals (mm d^{-1}) for the study period. Details of exact locations of hydrological measurements can be found in Heppell et al. (2016a, 2016b).

Temperature, pH, dissolved oxygen (optical) and electrical conductivity of river water were logged in-situ at 30 mins intervals using a Water Quality Multiprobe (Manta 2, Eureka Water Probes, USA). An automatic water sampler (6712, Teledyne ISCO, USA) collected water samples from the river every 48-hrs from June 2013 to June 2014 for analysis of water chemistry, and samples were collected fortnightly. Therefore, field and laboratory tests were undertaken to ensure that sample degradation over this time period was negligible. Furthermore, MilliQ water was decanted into sample bottles in the field to create field blanks to ensure no sample contamination occurred during transportation between the field and laboratory. Three riparian piezometers (screen depth installed in the soil C horizon, typically circa. 2 m depth) with porewater sampling tubes at screen depth were installed in the banks at each site in summer 2013 to enable measurements of riparian hydraulic head and porewater samples to be collected for chemical analysis. Hydraulic head was measured using pressure transducers (HOBO U20-001-01, Onset Corporation, USA at AS, GA and GN; Levelogger Edge, Solinst, Canada at CE) validated with manual dips on a fortnightly basis. Porewater samples were collected from sampling tubes on the riparian piezometers every two months from February 2014 to June 2016 using a syringe and tygon tubing. Samples were then filtered to 0.45 μm in the field.

Sites AP and CW were a component of the Demonstration Test Catchment network (McGonigle et al., 2014; Outram et al., 2014). At AP, stream discharge was measured using a Mace Flow Pro to record paired stage height and velocity measurements at 15-min temporal resolution to which the velocity-area method was applied (Lloyd et al., 2016a,b). The Mace Flow Pro measurements were taken within a concrete section which meant that the cross-sectional area was stable. However, during high flow events, the stage height overtops the concrete structure and out of bank flows occur. In these cases, a weir equation was implemented to account for the additional water flowing over the concrete section:

$$Q_i = C_d b H_i^{1:5}$$

where: Q_i is the discharge at time point $_i$ (m^3 s^{-1}), C_d is the dimensionless coefficient of discharge, b is the weir crest breadth (m) and H_i is the stage height (m) above the bridge at time point $_i$. C_d was set at 2.7 based on typical values from published literature (Brater and King, 1976). Discharge data for CW were obtained from the Environment Agency Gauging Station (Gauge number 43,806), which provided 15-min resolution stage height data using a Thistle 24R Incremental Shaft Encoder with a float and counterweight. For periods of modular flow, these data were used in conjunction with a stage-discharge curve to calculate discharge (ISO 1100-2, 2010). However, during non-modular flow periods, the stage heights are used alongside 15-min velocity measurements from a second ultrasonic gauge to calculate discharge using the velocity-area method (ISO 1088, 2007). At both sites daily river water samples were collected using automatic water samplers (Teledyne ISCO 3700, USA) and collected weekly.

2.3 Laboratory analysis

On return to the laboratory a sub-sample of river water from sites AS, GA, GN and CE was filtered at 0.45 µm for analysis of nitrate and DOC. Nitrate concentrations were analysed using ion exchange chromatography (Dionex-ICS2500). The limits of detection (LOD) and precision were 8 µmol L^{-1} ± 7 %. These samples were then prepared for DOC analysis by acidification to pH < 2 with HCl and then analysis by thermal oxidation (Skalar) using the non-purgeable organic carbon (NPOC) method. The LOD of the DOC analysis was 42 µmol L^{-1} with precision of ± 12 %. Accuracy was ensured by analysis of certified reference material (SPS-SW2 and TOIC4M14F1 for nitrate and DOC respectively) with each instrument run. Porewater samples from all sites were analysed using the same methods as for the surface water from AS, GA, GN and CE.

River samples collected from sites AP and CW were filtered then analysed for nitrate using a Skalar San++ multi-channel continuous flow autoanalyser. This analysis was based on the hydrazine-copper reduction method producing an azo dye measured colorimetrically at 540 nm. DOC was analysed as non-purgeable organic carbon by coupled high temperature catalytic oxidation using a Shimadzu TOC-L series analyser. For further details on sample collection and analysis at AP and CW sites see Yates et al., 2016.

2.4 Data analysis

BFI (BFI) for each site was calculated using the hydrograph separation procedure outlined in Gustard et al. (1992). Hydrographs with high BFI show relatively smooth characteristics and are indicative of major aquifers where water (and consequently solute) residence time in permeable bedrock will be of the order of decades whereas a low BFI is characterised by a flashy hydrograph, with steep recession curves, and is indicative of a generally shorter residence time in the catchment before water reaches the stream channel, with quickflow comprising shallow, lateral preferential and overland pathways predominant during storm events. Soil moisture deficit (SMD) is defined as the amount of water (in mm) which would have to be added to the soil in order to bring it back to field capacity. SMD values were obtained from the UK Meteorological Office for MORECS square 169 (4000 east, 1400 north) for a medium textured soil type with predominantly grass cover.

In order to quantify the relationships between nitrate, DOC and DOC:nitrate molar ratio with BFI, and to understand how any relationship varied intra-annually a linear mixed effects modelling approach was used. Linear mixed effects models account for missing data, which is a common issue associated with long-term field datasets, and the inclusion of repeated measures in the analysis (Blackwell et al., 2006). The 'lmer' function in R (R Core Team, 2016) package lme4 (Bates, Maechelr & Bolker, 2015) was used to perform a linear mixed effects analysis of the relationship between BFI as the independent measure, and either nitrate concentration, DOC concentration or DOC:nitrate molar ratios as the dependent variable. The nitrate and DOC concentration of river water recorded at each site over the same time period (i.e. from samples collected at simultaneous 48-hr time intervals from June 2013 until June 2014) was used in the analysis. BFI was entered as a fixed effect. We accounted for the influence of repeated measures by including time (Julian Day) as a random intercept and slope in the model. The 'lme' function in R package 'nlme' (Pinheiro et al., 2016) was used to fit a linear mixed effects model to porewater data to investigate differences in nitrate and DOC concentrations between CE and CW (the Chalk sites) and all the other sites (AS, AP, GA and GN).

For the purposes of considering the relationship between BFI and nitrate concentrations in the wider Hampshire Avon catchment, nitrate concentrations in river water samples collected between June 2013 and June 2014 were obtained from the Environment Agency Harmonised Monitoring Scheme (HMS) Records. Average annual nitrate concentration was calculated for each site, but those with less than 12 samples in the 12-month period were removed from the analysis (number of samples ranged from 12 to 56 depending on the site). BFI for each Environment Agency site was estimated using the Flood Estimation Handbook which uses the Hydrology of Soil Types (Boorman et al., 1995) methodology because there is not a gauging station at every location. Baseflow indices derived in this manner are referred to as BFIHOST to distinguish them from BFI values derived using our own discharge data. Pearson correlation analysis was used to explore relationships between solutes (nitrate and DOC) and BFI.

Annual loads of nitrate and DOC for sites AS, GA and CE were calculated as kg ha^{-1} by integrating paired concentration and discharge data collected on a 48-hr basis from June 2013 to June 2014. Any missing solute data (maximum gap of 10 days due to equipment failure) were infilled using seasonal concentration-discharge relationships derived for each site. Seasonal loads are expressed as a percentage of total annual load for each site.

3 Results

3.1 Rainfall and soil moisture deficit during the study period

The first year of study (June 2013-2014), on which these results are focused, was characterised by pronounced cycles of soil wetting and drying due to alternating periods of unusually wet and dry weather (Figure 2). Due to a combination of lower-than-average rainfall (c. 50% of 1910-2015 long term average for the region) and high temperatures (>28ºC for a 10-12 day period in July) over the summer of 2013, SMD reached a maximum of 140 mm for a 4 week period in August and September 2013. A period of unsettled weather in October and November 2013 (224 mm rainfall in total) reduced the SMD to 0 mm. After a brief return to dry, settled conditions, a series of deep Atlantic low pressure systems brought a prolonged period of heavy rain to the entire Hampshire Avon catchment. 161 mm rain fell in December 2013 (190% of the 1961-1990 long term average), with a maximum daily rainfall total of 58 mm on 23 December, followed by a further monthly total of 205 mm and 148 mm in January and February 2014, 261 and 259 % of the long-term averages, respectively. January 2014, in particular, was the equal-wettest on record since 1910. SMD and rainfall patterns in 2014 were not as extreme as those in 2013, returning to monthly values that were much closer to the long term averages. SMD reached peak values of 129 mm by the end of the summer in early October 2014, and autumn rainfall during October and November caused wetting up of the soil to reduce SMD to 0 mm by mid-November 2014. By March 2015, warmer weather, combined with lower-than-average rainfall (< 50% of long term average) caused SMD to steadily increase until the end of the study period in June 2015.

3.2 Quantification of the relationship between BFI and nutrients

Nitrate concentration in surface water of our sub-catchments is significantly positively correlated with BFI ($r=0.749$, $p<0.001$), whereas DOC concentration in our surface water samples exhibits a significant negative correlation with BFI ($r=-0.881$, $p<0.001$) (Figure 3a & 3b, Table 2). The linear mixed effects model analysis indicates that BFI has a significant effect on nitrate ($\chi^2(1)=19$, $p<0.0001$) and DOC ($\chi^2(1)=497$, $p<0.0001$) concentrations, with an increase in BFI of 0.5 leading to a difference in average increase in surface water nitrate concentrations of 260 μmol L^{-1} and a reduction in DOC concentrations of 840 μmol L^{-1} between the clay and Chalk sites. Inclusion of time as a random effect (both slope and intercept) improved the model fit for both nitrate and DOC, indicating that temporal dynamics associated with these determinands are important to consider. The sites of lower BFI exhibit marked variations in nitrate concentration in autumn and winter, which change the slope (although not the overall direction) of the nitrate and BFI relationship, and highlight the importance of seasonality. Overall, the respective increase in nitrate, and decrease in DOC concentration with BFI, broadly reflects the patterns in concentrations of DOC and nitrate in the riparian zones associated with each geology. Nitrate concentrations in riparian porewaters were significantly higher in the Chalk sites compared to the clay and Greensand sites ($F_{(1,146)}=105$, $p<0.0001$), whereas DOC concentrations were significantly lower in the Chalk sites compared to the others ($F_{(1,146)}=38$, $p<0.0001$). The relationship between DOC:nitrate molar ratio and BFI is non-linear and can be best described by a power function ($(\text{DOC:nitrate})=0.453*\text{BFI}^{-2.575}$, $r^2=0.638$, $p<0.001$, Figure 3c).

The relationship between nitrate and BFIHOST was tested for 17 additional sites within the Hampshire Avon catchment using Environment Agency Harmonised Monitoring Scheme data collected between June 2013 and June 2014. Figure 4a shows that across the Hampshire Avon, there is a significant, positive, linear relationship between nitrate and BFIHOST ($r=0.951$) with a regression model indicating that BFIHOST accounts for 90.4% of the variation in nitrate concentration. There is also a significant, positive correlation between nitrate concentration and % arable land use ($r=0.839$, $p<0.001$). Although % arable and BFIHOST are positively correlated (r=0.881), a tolerance value (a test for collinearity) of 0.224 indicates that multiple linear regression can be used in this instance (Field, 2000). Multiple regression shows, however, that BFIHOST alone produces the best model, with the forced inclusion of % arable resulting in no significant improvement to the model fit (Table 2).

3.3 Intra-annual variations of groundwater and quickflow contribution.

From this point forward, data from three sites only are presented as illustrative of the hydrochemical signatures from a range of BFIs across our three geologies; Chalk (Site CE – high BFI), Greensand (Site GA – intermediate BFI) and clay (Site AS – low BFI). There is a marked difference in the response of electrical conductivity to discharge across the three sites (Figure 5a-c). At the chalk site, CE, a maximum electrical conductivity of 0.570 mS cm^{-1} is maintained across the full range of recorded discharge. At the Greensand site, GA, electrical conductivity is maintained at c. 0.650 mS cm^{-1} until discharge exceeds 1 mm d^{-1} and then a decline in electrical conductivity with increasing discharge is observed. An examination of electrical conductivity by season indicates that geogenic solute concentration was lowest at the Greensand site during winter 2014, and concentrations were comparable in spring, summer and autumn (Figure 5b). At the clay site, AS, there are two different relationships between electrical conductivity and discharge; a constant electrical conductivity of c. 0.520 mS cm^{-1} is maintained at lower discharges of 0.001 – 0.3 mm d^{-1}, whilst a log-linear decrease in electrical conductivity is observed between 0.2 and 3.5 mm d^{-1}, and there is some overlap between the two patterns of behaviour. Box-plots of electrical conductivity by season indicate highest concentrations of geogenic solutes in summer, intermediate concentrations in autumn and spring, and lowest concentrations in winter (Figure 5c).

Inter-site comparisons of the response of nitrate, DOC and DOC:nitrate molar ratio to variations in discharge are illustrated in Figure 6. There is a significant, positive correlation between log-nitrate and log-discharge for all sites, with the slope of the regression relationship increasing with BFI (CE<GA<AS; Table 3). Visual examination of the relationship between nitrate and discharge for AS and GA

suggests more than one trend is apparent and this is investigated in detail by considering seasonality below. There is also a significant, positive correlation between log-DOC and log-discharge, although in this case the slope of the regression relationship increases in the following order: AS<CE<GA (Table 3). However, again there is marked scatter in the relationship and this is investigated further below. There is a similar significant, proportional increase in DOC:nitrate molar ratio with increasing discharge at both CE and GA (slopes of 0.199 and 0.196, respectively on a log-log basis, Table 3) whilst AS has a much weaker relationship, exhibiting far greater scatter.

3.4 Seasonality of concentration-discharge relationships for three selected sites

Nitrate concentrations at the Chalk Site, CE, show little variation with season or discharge, whereas DOC concentrations appear to follow two trends; (i) a slight increase in DOC concentration with discharge in spring and winter; and (ii) elevated concentrations of DOC which are unrelated to discharge in spring (Figure 7a). Consequently, DOC:nitrate molar ratios remain low (<1) throughout the year (Table 4).

At the Greensand site, GA, both nitrate and DOC concentrations increase with discharge (irrespective of season) until a breakpoint is observed at 1.5 mm d^{-1}. At this point, during the winter storms of 2013-14, nitrate concentrations start to decline with increasing discharge whereas DOC concentrations drop to < 500 μmolL^{-1} and a new, positive trend in increasing DOC with increased discharge is observed with a gentler slope (Figure 7b). As a consequence, the positive relationship between DOC:nitrate ratios and discharge also show a similar breakpoint, but the DOC:nitrate ratio remains below 3:1 throughout the year (Table 4).

At the clay site, AS, there are two trends in the concentration-discharge relationship for nitrate (Figure 7c). Concentrations are highest (200-400 μmol L^{-1}) during the autumn storms of intermediate discharge that followed the summer drought of 2013.

The winter storms of 2014 are associated with highest discharge, but lower nitrate concentrations (c. 100 μmol L^{-1}). This contrasts with DOC which shows a plateau in concentration (c. 1000 μmol L^{-1}) with increasing discharge, irrespective of season. Nitrate and DOC concentrations were plotted against electrical conductivity to test whether nitrate and DOC arose from a linear combination of old (long residence time) and new (short residence time) water, but this was not the case (data not shown) suggesting that variations in supply and/or in-stream processing of these solutes occur through the seasons. At AS, there are two observable trends in DOC:nitrate molar ratio: (i) highest and the greatest variability in DOC:nitrate ratios are observed during summer low flow conditions; (ii) there is an increase in DOC:nitrate ratios with discharge irrespective of season (Figure 7d). Consequently, during autumn, values of DOC:nitrate ratios were generally equal to or less than five, whilst values significantly greater than the threshold of four observed by Taylor and Townsend (2010) predominated during spring, summer and winter (Table 4).

Over 50% of the annual DOC load was exported from our sub-catchments during winter months, irrespective of geology. In the spring, 22-28% of the annual DOC load was transported, with summer and autumn months together responsible for < 20% of the total weight of DOC leaving each sub-catchment (Table 4). Winter was also an important season for nitrate export with between 45 and 66% of the total annual nitrate load being exported. Spring export of nitrate was important in both Chalk and clay sub-catchments (c. 30% of annual load) and in the clay, autumn export of nitrate was also of comparable magnitude to spring (Table 4).

4 Discussion

4.1 Contrasting hydrological responses across a gradient of BFI

Our six sites exhibit a range of BFI (0.207-0.905) indicating a gradient from river water with 80-90% groundwater contribution to total flow in the chalk geology, 70-80% groundwater contribution in the Greensand and only 20-55% groundwater characteristic at the sites underlain by clay geology. Our calculation of BFI for the six sites, based on our two-year discharge dataset, compared favourably with the BFI estimated from HOST (Gustard et al., 1992).

BFI and logEC-logQ plots are useful complementary approaches to interpreting hydrological and hydrochemical pathways operating in the sub-catchment associated with each site. Electrical conductivity is an aggregated measure of geogenic solute response in the sub-catchment, and provides an indication of relative contributions of old groundwater (long residence time) and new (short residence time) water arising from routes such as shallow throughflow, preferential pathways and overland flow to the river. The study allowed the full range of flows at the sites to be sampled because two extreme conditions in the UK were captured: the summer drought of 2013 and the extremely wet winter of 2013-2014. In the Chalk, the logEC-logQ plots show groundwater (old water) dominance during the period of flooding, because electrical conductivity is maintained through the entire range of flows, including at the highest discharge approaching 10 mm d^{-1}. At the Greensand site, the sharp decline in electrical conductivity at discharges >1.5 mm d^{-1} provides evidence of dilution of total dissolved solutes by new water, which occurs only during the wet winter of 2014. At the clay site, EC-Q relationships demonstrate that quickflow pathways, most likely involving preferential delivery enabled by field drainage (both agricultural and army camp drains from World War II) installed due to the risk of seasonal waterlogging on the slowly permeable local clay soils (Denchworth and Wickham soil series), are operational throughout autumn, winter and spring months. Under summer baseflow conditions, the field drains are inactive and any river flow (almost negligible during the summer drought of 2013) is provided by springs draining the aquifers of the Upper Greensand and Wardour Formation (Allen et al., 2014), or direct discharges from septic tanks, and drains connecting farm yards to the stream.

4.2 Nitrate and DOC concentrations as a function of BFI

Average annual nitrate concentrations in surface waters of the Hampshire Avon catchment increase with increasing BFI. In a UK-wide study, Davies and Neal (2007) used linear regression to consider how catchment characteristics control mean nitrate concentrations in UK rivers. Nitrate concentrations were explained by land use (% arable and % urban), topography (expressed as % upland), effective rainfall (mm) and BFI. Therefore, on the basis of these prior national analyses, it would be predicted that % arable and BFI would be the most important explanatory factors. For the Hampshire Avon, stepwise regression analysis showed limited co-linearity between BFI and % arable, and forced entry regression indicated that BFI was the better explanatory variable for mean nitrate concentrations. In the UK, historical fertiliser applications have led to elevated concentrations of nitrate in both Chalk and Upper Greensand aquifers; currently in the range 500-645 μmol L^{-1} (Defra, 2002; Burt et al., 2011; Howden et al., 2011; Wang et al., 2016). Although the Chalk aquifer of the Hampshire Avon has been designated as a Groundwater Nitrate Vulnerable Zone (NVZ) under the EU Nitrate Directive (Directive 2000/60/EC), the time taken for water to move from the soil surface, through the unsaturated zone to the aquifer can result in a decadal scale time-lag between implementation of management practice and any observed response in groundwater or river nitrate concentrations (Allen et al., 2014; Wang et al., 2012). We observe an increase in nitrate load in baseflow with increasing BFI (Chalk > Greensand > clay) in line with previous research by Tesoriero et al (2013), and our riparian porewater samples indicate significantly higher nitrate concentrations in the soil C horizon of the Chalk sites in comparison to Greensand and clay sites. However, it is an over-simplification to suggest that the gradient of annual average nitrate concentrations with BFI can be explained solely by different ratios of nitrate-rich groundwater to relatively nitrate-poor quickflow components of the hydrograph over an annual cycle. If this were the case, then nitrate concentrations would be highly correlated with electrical conductivity, and they are not. Instead, our analysis suggests that additional N transformation processes, and exchange with other N species forms instream, driven by seasonality and varying land use and management contribute to the observed patterns that we see, and this is discussed below.

Our six sites provide evidence that average annual DOC concentrations decline with increasing BFI in the Hampshire Avon catchment. Unfortunately, the Environment Agency does not collect DOC data in the rivers of the Hampshire Avon region so we cannot investigate the wider applicability of the DOC trend. Wetland area is often cited as an important control on DOC concentrations in a catchment (Morel et al., 2009), but our sub-catchments all comprise < 0.6% wetlands by area. Data from the Environment Agency indicate that groundwater concentrations of DOC in the catchment are generally < 83 μmol L^{-1}. Porewater samples from the grassland riparian zone at each site show elevated DOC concentrations in comparison to regional groundwater, and the Chalk sites (high BFI) have significantly lower DOC concentrations in soil C horizons compared to the Greensand and clays, suggesting that soil type and underlying geology could influence the concentration at which DOC is delivered to the stream in these sub-catchments. Once again, DOC concentrations in the surface water cannot be explained by a mix of old and new water alone, and seasonality plays an important role in controlling the flux of DOC through river water.

4.3 Seasonal controls on nitrate and DOC export

The Chalk site (CE) is near-chemostatic with respect to total dissolved solutes and nitrate. This means that the absolute 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. It has been suggested that chemostatic behaviour for nutrients arises if sources accumulate in the landscape e.g. as legacy of nitrate management (Basu et al., 2010). Here nitrate has accumulated in groundwater (Wang et al., 2016) and it is the dominance of this old water under high discharge that gives rise to the near-chemostatic effect and transport-limited system. DOC is also transport rather than supply limited at this site, showing a slight increase in concentration with increasing discharge, and a more pronounced increase in spring which is not associated with a rise in discharge. In fact all three sites – on Chalk, Greensand and clay – have elevated DOC concentrations in spring, which could arise from production, leaching and export of DOC from catchment soils as soil temperatures rise (Aubert et al., 2013), and/or in-stream production.

At the Greensand site, there appears to be a threshold of discharge of c. 1.5 mm d^{-1} in winter above which there is evidence of different hydrological flowpath(s) or sources of water to the river with lower electrical conductivity compared to other seasons. Riparian head is closely correlated with discharge and shows two distinct regions of linearity which converge at a discharge of between 1 and 1.5 mm d^{-1}. At this threshold, riparian head is at 60-80 cm below the ground surface suggesting that the water table is at the base of the soil C horizon. As the water rises up through the soil horizons during the winter, the electrical conductivity in the river water drops indicating a supply of new water from soil in the riparian zone and potentially from the surrounding fields. Conceptualisations of solute transport from other researchers include differing contributions from near stream riparian areas with rising and falling groundwater, arising from a combination of soil solute concentration and near-stream lateral water flux (Prior and Johnes, 2002; Seibert et al., 2009), and/or increased connectivity and fraction of active catchment contributing water, with emphasis on the lateral dimension (Basu et al., 2010). Above the threshold of 1.5 mm d^{-1} the DOC and nitrate concentrations in the river reflect a combination of groundwater contribution and the depth-integrated mass flux of each solute from the soil A, B and C horizons. The reason for a decline in nitrate concentrations in river water above the threshold, whilst DOC concentrations increase, can be ascribed to the different depth-distributions of nitrate and DOC pools in the soil. The extent of the lateral connectivity between surrounding fields, the riparian zone and the river channel in these low gradient, intermediate BFI systems is not well characterised, and should be an area of further study.

Our two clay sub-catchments are dominated by artificially drained soils of the Kimmeridge Clay Series, and the field under-drainage will be a major control on the hydrological and hydrochemical response of the river. This is evident in the rapid fall in electrical conductivity in response to rainfall events (Figure S1) and in the variation in electrical conductivity with season which arises from the mix of rapid (via drainflow) and slow pathways of water during storm events, and suggests that the drains operate through much of the year (spring, autumn and winter). Concentrations of DOC in the surface waters of the two clay sites (167 – 2000 μmol L^{-1}) are comparable to the range reported in drainage waters from permanent grassland in South West England (Sandford et al., 2013). Increases in DOC concentrations in drainage water during rainfall events have previously been explained as being due to increased lateral flows through the upper soil horizons (Neff and Asner, 2001), which are generally relatively carbon enriched compared to lower soil horizons. Here, flushing of DOC from soil aggregates and subsurface micropores contributes to rising concentrations during storm events (Jardine et al., 1990; Chittleborough et al., 1992). Sandford et al. (2013) reported molar DOC:nitrate ratios of 18-25 at times of highest DOC export in drainage water (which is at the upper end of our observations for surface water of our clay catchment), and they also found that the molar DOC:nitrate ratio increased with discharge. The comparability of results suggests that our findings may have wider applicability to other catchments of mineral soils dominated by drained grassland.

The elevated concentrations of nitrate observed in the River Sem in Autumn 2013 (Figure S2), 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 rapidly to the stream through shallow subsurface pathways connected to topsoil, as opposed to the Chalk sub-catchments where groundwater contributions of nitrate dominate.

4.4 Ecological significance of temporal variations in DOC:nitrate ratio across a gradient of BFI

Here, we have shown that for our six tributaries of the Hampshire Avon, DOC:nitrate ratios are negatively correlated with BFI, but the relationship is non-linear. As far as we are aware, we are the first to demonstrate such a relationship, which, if more widely applicable to other lowland, agricultural catchments, might provide a useful means of predicting annual-averaged riverine nitrate and DOC concentrations.

The molar DOC:nitrate ratios fall in the lowest range recorded across multiple land use types in the US LINXII study (Mulholland et al., 2015), but vary over two orders of magnitude, suggesting order of magnitude variations in whole stream nitrate uptake velocity in river reaches across our contrasting geologies (0.05-0.4 mm min^{-1};

see Figure 7 in Rodríguez-Cardona et al., 2016). Nitrate uptake velocity is the vertical movement of nitrate to the riverbed measured using the whole stream 'Tracer Additions as Spiraling Curve Characterisation' method. The metric represents nitrate uptake efficiency, and can be interpreted as whole stream nitrate removal through, for example, denitrification and/or assimilatory processes, although the method does not allow for discrimination of these processes. On the basis of the relationship between DOC:nitrate and BFI demonstrated in this study, we can hypothesise that the clay sub-catchments are associated with higher whole stream nitrate removal than our Greensand and Chalk systems. Although we have no direct measurements of whole stream nitrate removal for these sites, we have measured in-situ rates of nitrate removal in the riverbed at these six sites using a modified push-pull technique (Jin et al., 2016), and the highest rates of nitrate removal were found at the two clay sites (see Table 4 in Jin et al., 2016). Whether DOC:nitrate ratios control nitrate removal may also depend on the net heterotrophic or autotrophic nature of our sub-catchments. In a net autotrophic reach, nitrate removal might correlate with physical factors such as light and temperature, which control photosynthetic activity, and hence the in-stream production of labile carbon which, in turn, is then tightly coupled to nitrate reduction. In contrast, in a net heterotrophic reach in our lowland, arable landscape, nitrate removal may depend on DOC:nitrate ratios driven by hydrological pathways delivering labile dissolved organic and inorganic carbon (Rodriguez-Cardona et al., 2016).

This study, amongst others, has revealed significant differences in the relationship between DOC:nitrate and discharge dependent on both geology and seasonal effects (Tiemeyer & Kahle, 2014; Thomas et al., 2016). The Chalk site exhibited little variation in DOC:nitrate with discharge due to the dominance of groundwater contribution at both high and low flows. At the Greensand site, there is a linear increase in DOC:nitrate with discharge irrespective of season. However, during the elevated flows in the winter, when riparian and rain water contributes increasingly to the discharge, causing a drop in electrical conductivity, a sharp change in nitrate and DOC concentration is observed resulting in an overall drop in DOC:nitrate during a time when > 66% of the total nitrate export occurs. In contrast at the clay site, lowest DOC:nitrate values and highest nitrate concentrations are associated with autumn storms of intermediate discharge, which export 26% of total annual nitrate load. These trends highlight contrasting seasons of risk associated with high nitrate export in combination with low DOC:nitrate ratios at the Greensand and clay sites. 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.

5 Conclusions

We have shown that the dynamism of hydrological pathways, here quantified using BFI, is a controlling factor influencing both annual average DOC and nitrate concentrations in heavily managed agricultural landscapes.

- In the Chalk sub-catchment, a near-chemostatic nitrate response over the year is a consequence of the dominance of nitrate-rich groundwater-flow, and nitrate export is transport-controlled. Thus, under future climate change scenarios, periods of groundwater flooding such as observed in winter 2013-4 will be critical periods of nitrate export with little opportunity for in-stream nitrate processing and removal due to a combination of short residence times, low water temperatures and low DOC:nitrate ratios (<0.5).
- In sub-catchments of intermediate BFI, such as the Greensand sub-catchments in this study, high winter flows, although arising from a mix of slow and rapid hydrological pathways, may also be characterised by water with low DOC:nitrate ratios circa. 1, suggesting that nitrate accrual rather than in-stream nitrate removal could be promoted downstream.
- Although heavily managed, the clay sub-catchment showed marked variation in nitrate and DOC concentrations with discharge, driven by season. In this sub-catchment there was a strong positive relationship between DOC:nitrate ratio and discharge, and DOC concentrations were generally higher than for our other landscape types. It seems that, at the landscape scale, both quickflow and preferential flow through field drains may supply rivers with a source of water conducive to promoting in-stream nutrient removal. Although

care should be taken to ensure that in such catchments, relatively high DOC concentrations do not arise from pollutant sources with a high biochemical oxygen demand (such as slurry), further work should focus on the sources and lability of DOC from drained, grassland soils.

At the landscape scale, it can be hypothesised that the locations where water from impermeable sub-catchments meet water from tributaries of lower BFI, may be hotspots of heterotrophic activity driven by upstream supply of water with a high DOC:nitrate ratio. 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 NVZs, or transitional and near-coastal areas.

Data Availability

Data are available to download from the NERC Environmental Information Data Centre (see links provided in Heppell et al., 2016a, 2016b). DTC data are available under an Open Government Licence from https://data.gov.uk/dataset/demonstration-test-catchments-data-archive.

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Table 1 Hydrological characteristics of the six sub-catchments in the Hampshire Avon.

Site code	Major geology	River	Stream order[a]	Catchment size (km^2)	BFI[b]	BFIHOST[c]	Major land use[d]
AP	Clay (>99%)	Sem	1(73%) 2(18%) **3**(9%)	4.9	0.207	0.234	Arable (5%), Grassland (95%)
AS	Clay (74%)	Sem	1(54%) 2(26%) **3**(20%)	26.0	0.549	0.372	Arable (10%), Grassland (90%)
GN	Greensand (52%)	Nadder	1(58%) 2(39%) **3**(3%)	34.6	0.781	0.695	Arable (46%), Grassland (33%)
GA	Greensand (50%)	W Avon	1(47%) 2(31%) **3**(22%)	59.2	0.744	0.861	Arable (25%), Grassland (50%)
CE	Chalk (96%)	Ebble	1 (28%) **2** (72%)	58.9	0.906	0.953	Arable (55%), Grassland (32%)
CW	Chalk (80%)	Wylye	1 (60%) **2** (40%)	53.5	0.901	0.931	Arable (50%), Grassland (35%)

[a] Strahler stream order with % contribution of stream order to the network and stream order at site in bold; [b] BFI calculated using discharge data collected from July 2013-2014; [c] BFI calculated using the UK Hydrology of Soil Types (HOST) classification; [d] Major Land use based on 2010 agcensus data

Table 2 Summary of (a) linear mixed effects model parameters; and (b) regression statistics.

<table>
<tr><th>Model</th><th colspan="2">Nitrate or DOC ~ BFI + (1 + BFI|Time)</th></tr>
<tr><td>Response variable</td><td>Nitrate</td><td>DOC</td></tr>
<tr><td>AIC</td><td>10752.7</td><td>10576.2</td></tr>
<tr><td>Fitting method</td><td>ML</td><td>ML</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>Random effects</td><td></td><td></td></tr>
<tr><td>Intercept (time)</td><td>7117</td><td>89601</td></tr>
<tr><td>BFI</td><td>10341</td><td>70703</td></tr>
<tr><td>Residual</td><td>11558</td><td>19051</td></tr>
<tr><td></td><td></td><td></td></tr>
<tr><td>Fixed effects</td><td></td><td></td></tr>
<tr><td>Intercept</td><td>-59.98</td><td>1668.2</td></tr>
<tr><td>Slope</td><td>520.62(±17.96)</td><td>-1679.55(±30.58)</td></tr>
</table>

Dependent	Independent	Correlation coefficient	Coefficient of determination	Slope (SE)	Intercept
Nitrate (17 sites)	BFIHOST	0.928	0.861***	535(47)	-45
Nitrate (17 sites)	% arable	0.839	0.704***	640(70)	130

Table 3 A summary of regression statistics for the relationships between log-Nitrate, log-DOC and log-Nitrate:DOC molar ratio by site with log-discharge.

Site	Dependent	R	R2	B (SE)
CE	Log(Nitrate)	0.263	0.069***	0.053 (0.014)***
	Log(DOC)	0.466	0.217***	0.254 (0.036)***
	Log-(DOC:Nitrate)	0.375	0.140***	0.199 (0.037)***
GA	Log(Nitrate)	0.742	0.550***	0.206 (0.014)***
	Log(DOC)	0.606	0.368***	0.403 (0.041)***
	Log-(DOC:Nitrate)	0.342	0.117	0.196 (0.042)***
AS	Log(Nitrate)	0.501	0.251***	0.361 (0.047)***
	Log(DOC)	0.542	0.294***	0.245 (0.029)***
	Log-(DOC:Nitrate)	0.176	0.031*	-0.110 (0.047)*

***p<0.0001; *p<0.05

Table 4 Export of nitrate and DOC expressed as % of total annual load at each site; and Mean DOC:Nitrate ratio (+/- SE) by season.

	Season			
	Summer	Autumn	Winter	Spring
Nitrate Seasonal Load (as % of annual)				
AS	3	26	45	26
GA	5	12	66	16
CE	6	4	57	31
DOC Seasonal Load (as % of annual)				
AS	6	11	55	27
GA	5	15	56	22
CE	4	2	64	28
DOC:Nitrate molar ratio				
AS	14.20 (0.81)	5.08 (0.64)	7.05 (0.45)	6.13 (0.43)
GA	1.36 (0.14)	1.47 (0.16)	1.19 (0.05)	1.69 (0.11)
CE	0.261 (0.01)	0.232 (0.03)	0.356 (0.03)	0.379 (0.03)

List of Tables

List of Figures

discharge for three sub-catchments of contrasting geology in the Hampshire Avon: Chalk - CE; Greensand - GA; and Clay – AS (June 2013 – 2014).

Figure 7. Seasonal variations in the relationship between nitrate, DOC and DOC:nitrate molar ratio with discharge for three sub-catchments of contrasting geology in the Hampshire Avon (June 2013-2014). (a) Chalk – CE; (b) Greensand – GA; (c) Clay – AS (d) Clay – AS.

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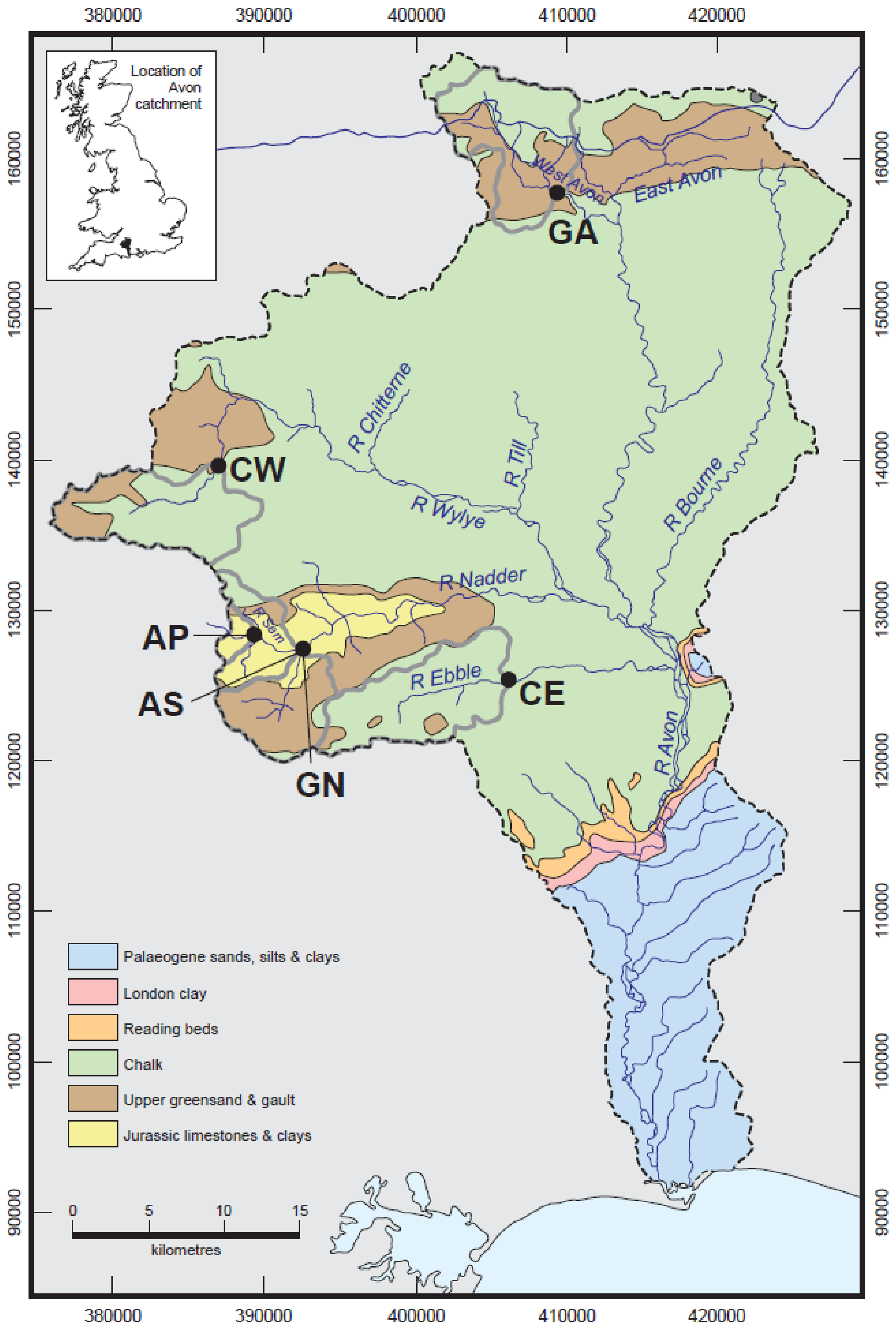


Figure 1. Catchment map of Hampshire Avon showing sites and geology. Grey lines indicate sub-catchment boundaries delineated by topography.

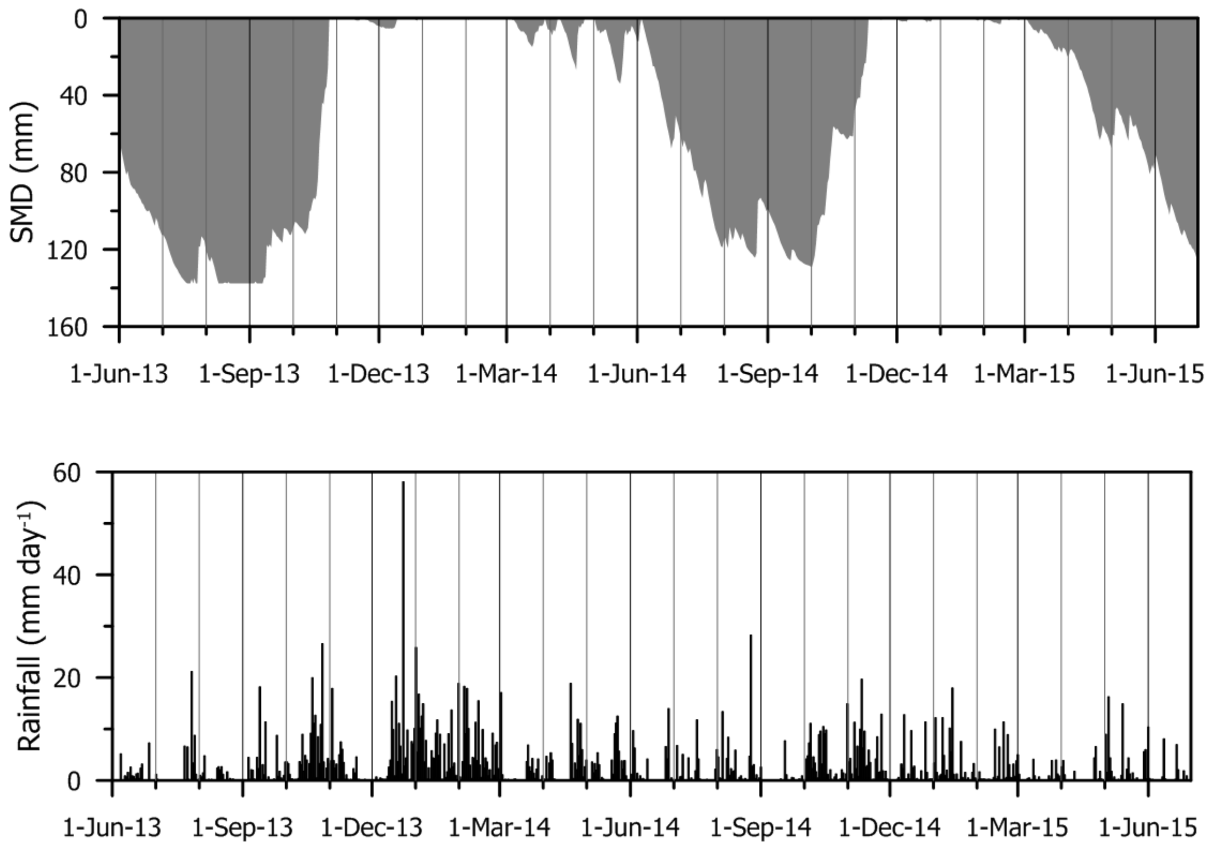


Figure 2. Soil Moisture Deficit (mm) and Daily Rainfall totals (mm) from June 2013 to June 2015.

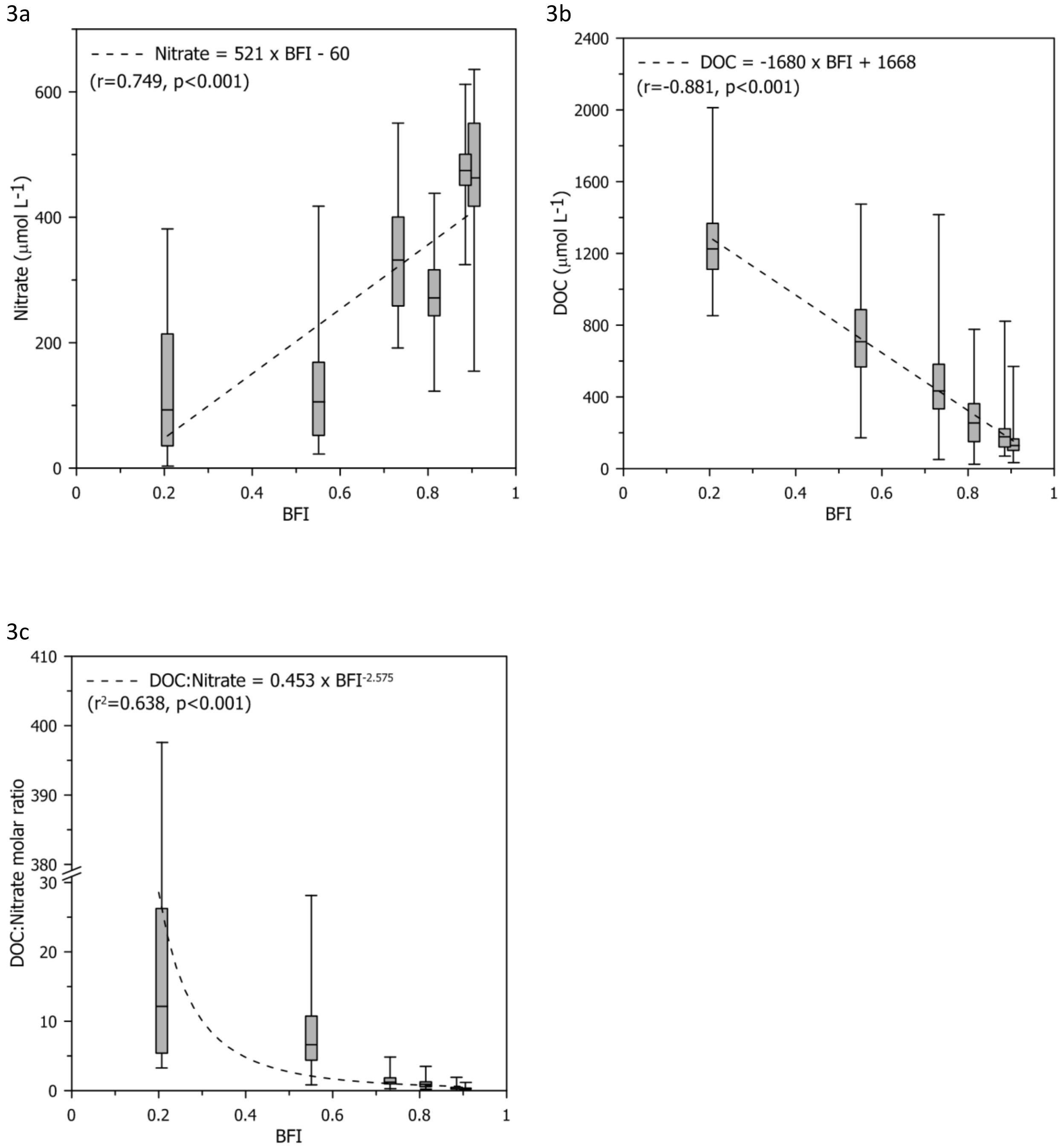


Figure 3. Relationship between (a) nitrate surface water concentration and BFI; (b) DOC surface water concentration and BFI; and (c) DOC:nitrate molar ratio and BFI for six sub-catchments in the Hampshire Avon.

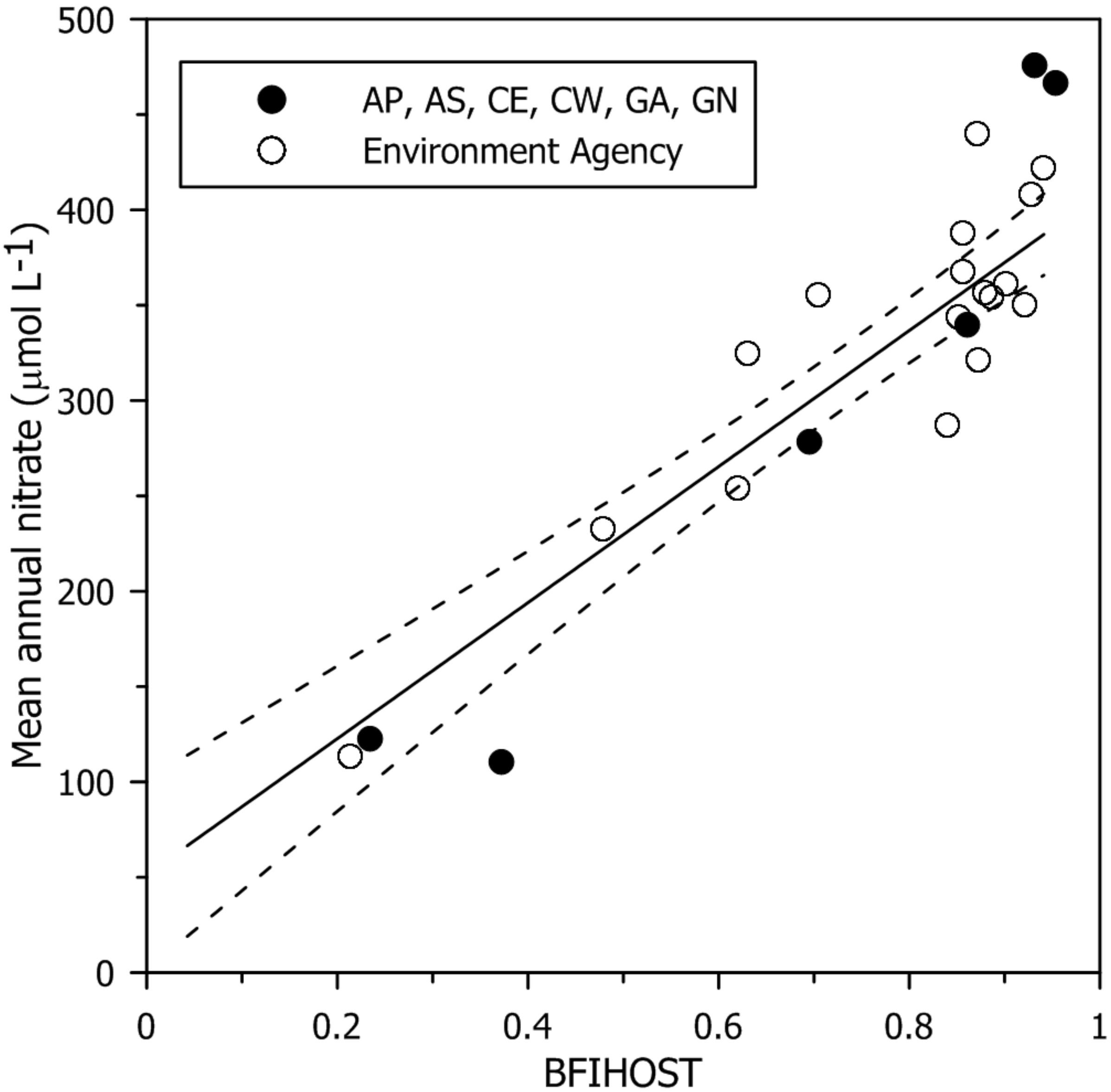
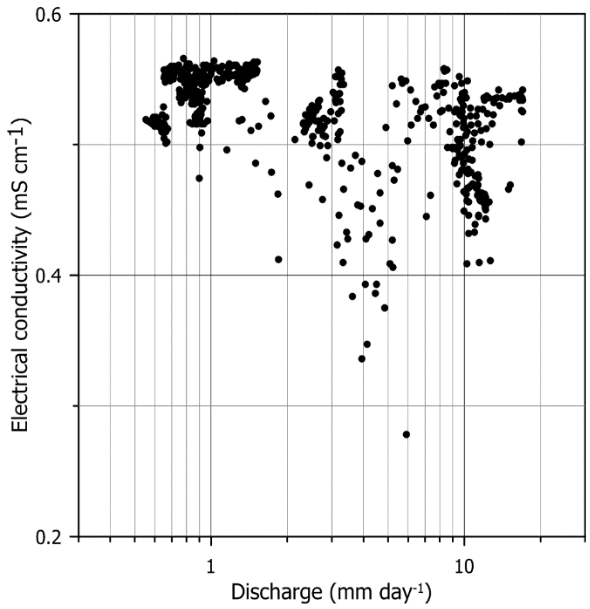


Figure 4. Relationship between nitrate concentration and BFI for this study and Environment Agency Harmonised monitoring sites upstream of Salisbury in the Hampshire Avon (June 2013 - 2014).



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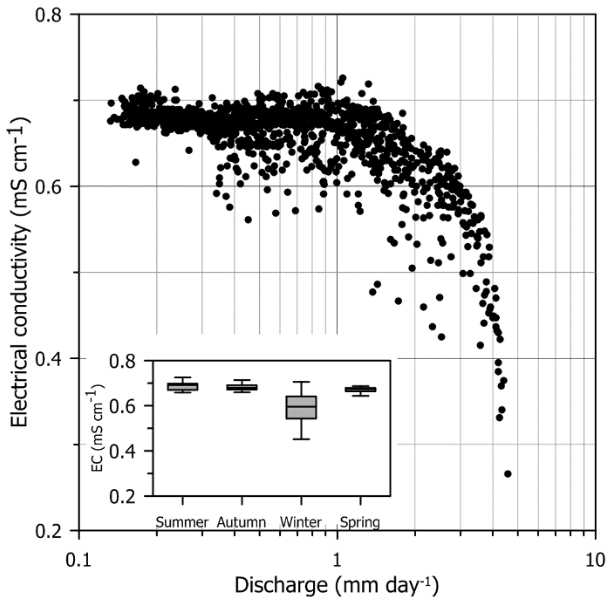

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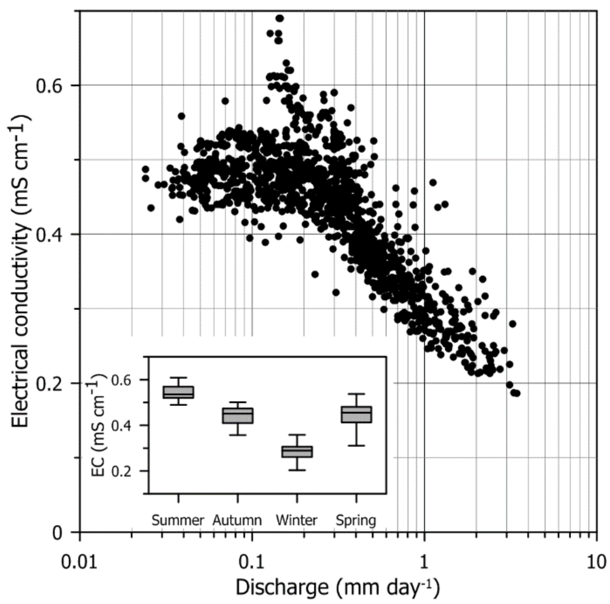

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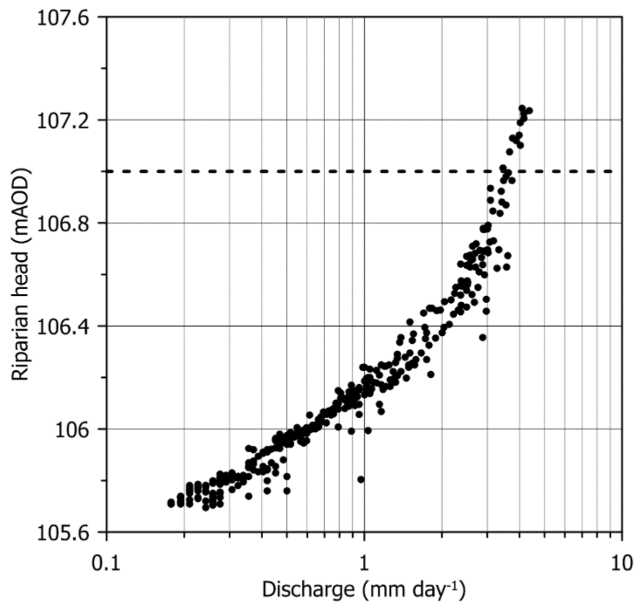

5d

Figure 5. Relationship between electrical conductivity and discharge for three sub-catchments of contrasting geology in the Hampshire Avon (a) Chalk - CE; (b) Greensand - GA; and (c) Clay – AS (June 2013 – 2015). Inset box-whisker plots indicate seasonal variations in electrical conductivity for Greensand (5b) and clay (5c) sites. 5(d) illustrates riparian head (mAOD) in relation to river discharge at Site GA.

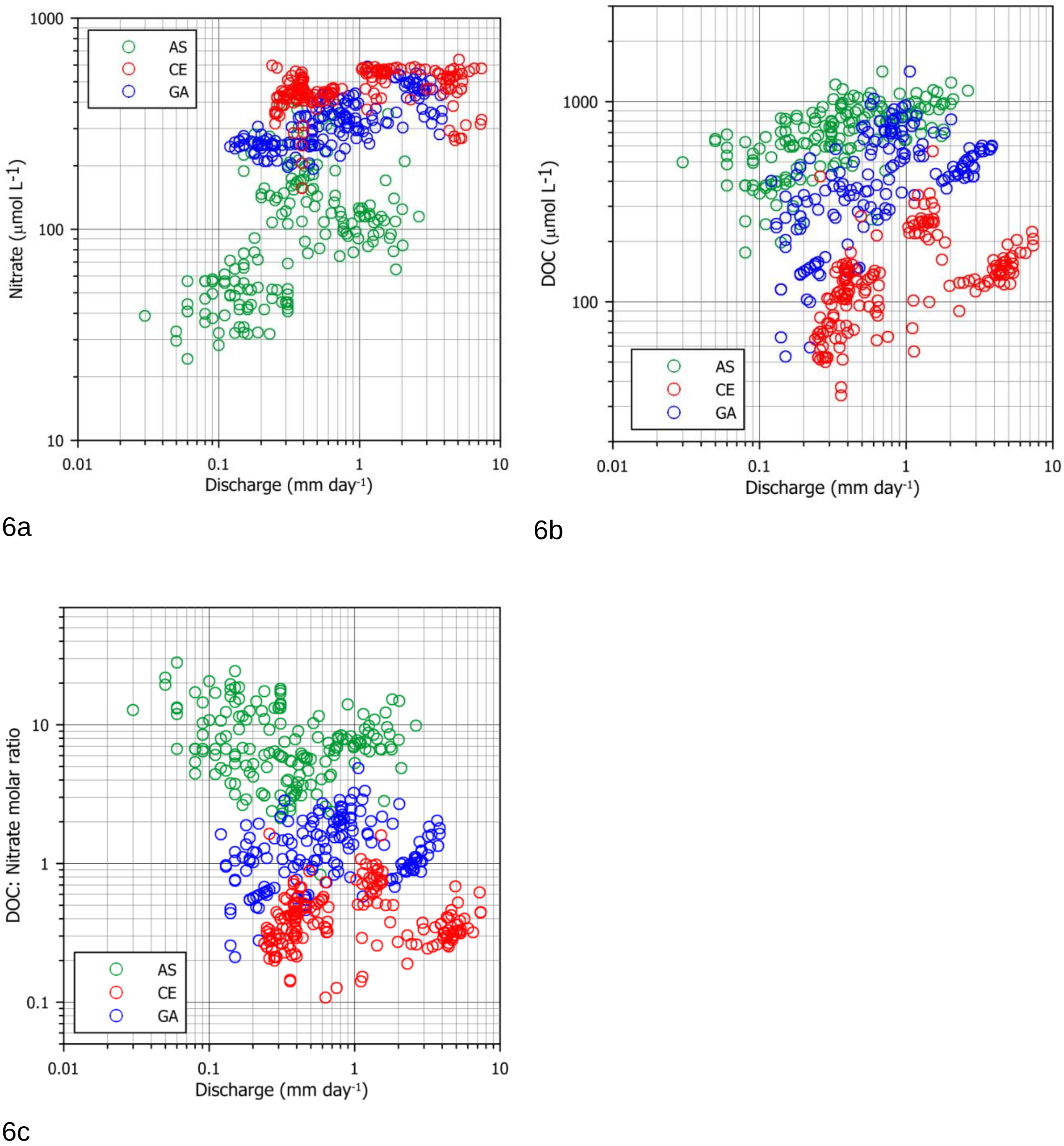

Figure 6. Inter-site comparison of the relationship between (a) nitrate concentration and discharge; (b) DOC and discharge; and (c) DOC:nitrate molar ratio and discharge for three sub-catchments of contrasting geology in the Hampshire Avon: Chalk - CE; Greensand - GA; and Clay – AS (June 2013 – 2014).

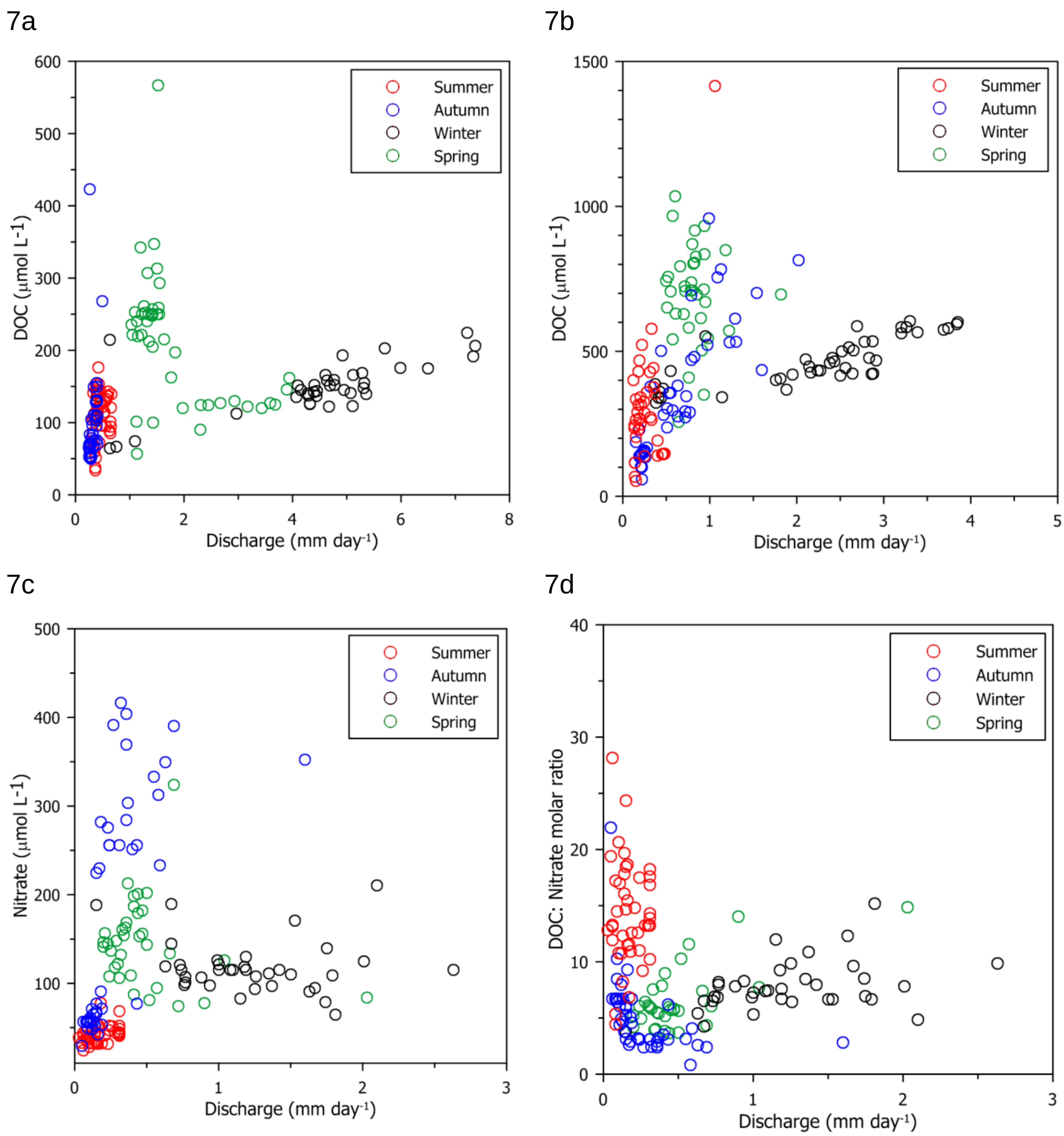

Figure 7. Seasonal variations in the relationship between solutes and discharge for three sub-catchments of contrasting geology in the Hampshire Avon (June 2013-2014). (a) Chalk – CE; (b) Greensand – GA; (c) Clay – AS (d) Clay – AS.