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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, yet important to assess given the potential changes to production and delivery of DOC and nitrate arising from climate change. 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 Baseflow Index (BFI) and DOC:nitrate molar ratios across

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contrasting geologies (Chalk, Greensand and clay). We found a significant positive relationship between nitrate and Baseflow Index ($p<0.0001$), and a significant negative relationship between DOC and Baseflow Index ($p<0.0001$), resulting in a non-linear negative correlation between DOC:nitrate molar ratio and Baseflow Index. 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 Baseflow Index 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 storm events in sub-catchments underlain by Chalk and Greensand, and autumn events in drained, clay sub-catchments) when DOC:nitrate molar ratios are low, suggesting low potential for in-stream uptake of inorganic forms of nitrogen. Future work should determine whether the results reported here are transferable to other agricultural, lowland catchments, and seek to understand the generalised hydrological controls on the availability of DOC transported through such landscapes.

1 Introduction

As we enter the Anthropocene, the increase in nitrogen 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 nitrogen 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 nitrogen 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 nitrogen 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.

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Across the UK, nitrate concentrations in rivers are controlled by land use, relative contribution of baseflow to streamflow and effective rainfall (Davies and Neal, 2007). The problem of excessive nitrate export and high nitrate concentrations arising from agricultural practice are most pressing in lowland catchments, such as the Hampshire Avon, the focus of this study. In agricultural catchments, possible management solutions need to be targeted to suitable scales of implementation, such as farms and sub-catchments (Collins et al., 2016; Johnes et al., 2007). Thus, our work considers different tributaries of the Hampshire Avon characterised by three geologies (Chalk, Greensand and clay) with a range of groundwater influence. Within this catchment, we predict that annual average nitrate concentrations will be positively correlated with Baseflow Index following the findings of Davies & Neal (2007) and we seek to establish any relationship between Baseflow Index and DOC, and between Baseflow Index and DOC:nitrate ratio.

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 ($C=AQ^b$), 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 within which we might hypothesise that groundwater dominated areas will exhibit a stable, more damped, hydrochemical response throughout the year, whereas sub-catchments of low Baseflow Index 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 catchment, 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:

(i) To quantify the relationship between nitrate, DOC and DOC:nitrate molar ratio with Baseflow Index for six sub-catchments of contrasting geology in the Hampshire Avon.
(ii) 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.
(iii) To quantify spatio-temporal differences in DOC:nitrate ratios in this agricultural landscape and assess the potential implications of these variations for future nitrogen 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 Baseflow Index (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 baseflow indices of 0.695 and 0.861, respectively. The two sites characterised by the lowest baseflow indices, 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 circa 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).

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Temperature, pH, temperature, 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 (3700, Teledyne ISCO, USA).

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

Baseflow Index (BFI) for each site was calculated using the hydrograph separation procedure outlined in Gustard et al. (1982). 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 Baseflow Index, 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. Baseflow index 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.

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 (>28^{o}C for a 10-12 day period in July) over the summer of 2013, soil moisture deficit (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 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 ($\chi^2(1)=19.348$, $p<0.0001$) and DOC ($\chi^2(1)=497.82$, $p<0.0001$) 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 (DOC:nitrate)=0.453*$BFI^{-2.575}$, 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 Contrasting hydrochemical signatures of three sites of low, intermediate and high BFI

From this point forward, data from three sites only are presented as illustrative of the hydrochemical signatures from a range of baseflow indices 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 $\mu molL^{-1}$ 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 $\mu mol\ L^{-1}$) 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 $\mu mol\ L^{-1}$). This contrasts with DOC which shows a plateau in concentration (c. 1000 $\mu mol\ L^{-1}$) 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 and new water, but this was not the case (data not shown) suggesting that variations in supply and/or in-stream processing of these solutes occurs 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 the 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, the data 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 nitrogen transformation processes, and exchange with other nitrogen 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.

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4.3 Seasonal controls on nitrate and DOC export

The Chalk site (CE) is chemostatic with respect to total dissolved solutes i.e. overall, the concentration of geogenic solutes is maintained at higher discharge, so that discharge drives solute load and hence the export of solutes to the coast. This observation also holds for nitrate. It has been suggested that chemostatic behaviour for nutrients arises if sources accumulate in the landscape e.g. as legacy of nitrate management. 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 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 mineralisation, 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 our 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 (data not shown) 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.

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.

This study has revealed significant differences in the relationship between DOC:nitrate and discharge dependent on both geology and seasonal effects. 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 and also suggests that periods of lateral flow from soils, 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, and thus the extent to which groundwater influence also affects DOC:nitrate ratios. In the Chalk sub-catchment, a 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

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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; and little evidence of chemostatic behaviour. 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 that have not as yet been fully explored but are important to understand, especially when receiving waters downstream are designated as Nitrate Vulnerable Zones, or where downstream transitional and near-coastal waters are impacted.

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] Baseflow Index calculated using discharge data collected from July 2013-2014; [c] Baseflow Index calculated using the UK Hydrology of Soil Types (HOST) classification; [d] Major Land use based on 2010 agcensus data

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

Model	Nitrate or DOC ~ BFI + (1 + BFI|Time)	
Response variable	Nitrate	DOC
AIC	10752.7	10576.2
Fitting method	ML	ML
Random effects		
Intercept (time)	7117	89601
BFI	10341	70703
Residual	11558	19051
Fixed effects		
Intercept	-59.98	1668.2
Slope	520.62(±17.96)	-1679.55(±30.58)

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)

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discharge for three sub-catchments of contrasting geology in the Hampshire Avon: Chalk - CE; Greensand - GA; and Clay – AS (June 2013 – 2015).

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. (a) Chalk – CE; (b) Greensand – GA; (c) Clay – AS (d) Clay – AS.

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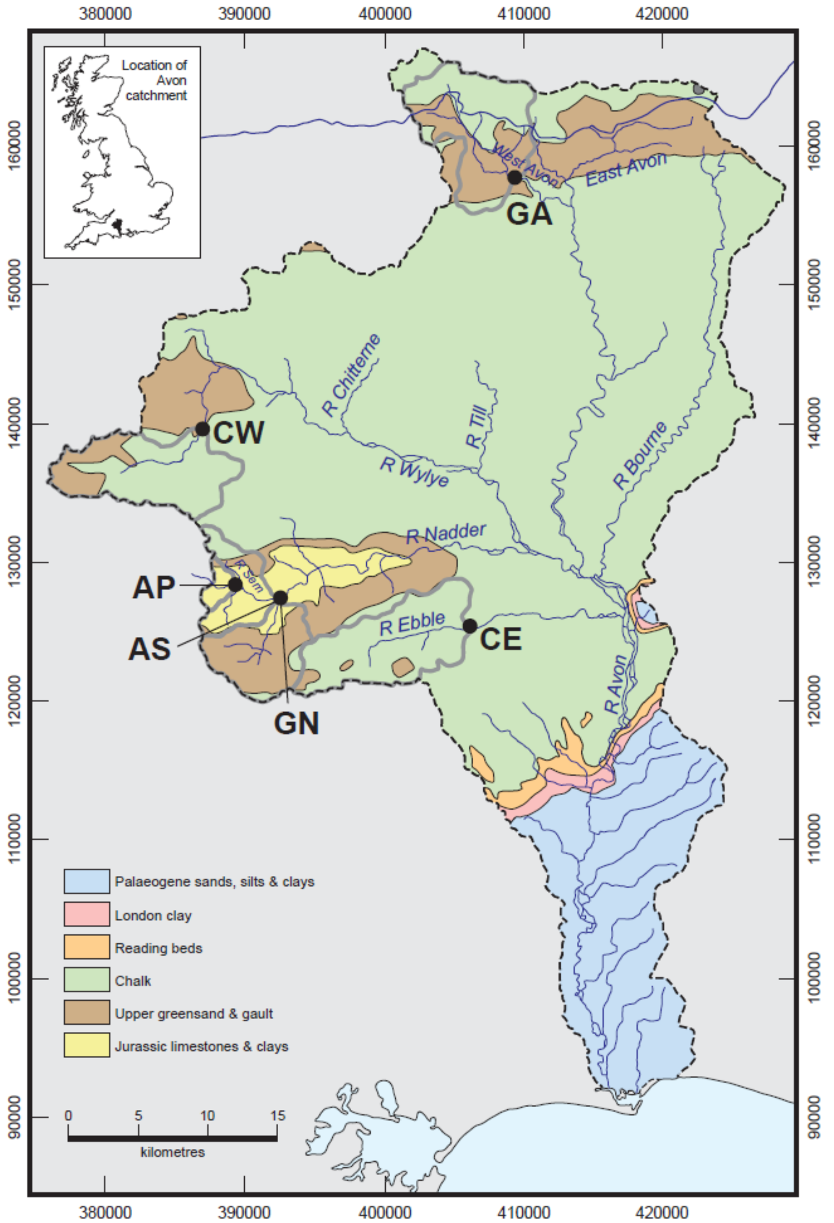

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1090 Figure 1. Catchment map of Hampshire Avon showing sites and geology. Grey lines
1091 indicate sub-catchment boundaries delineated by topography.

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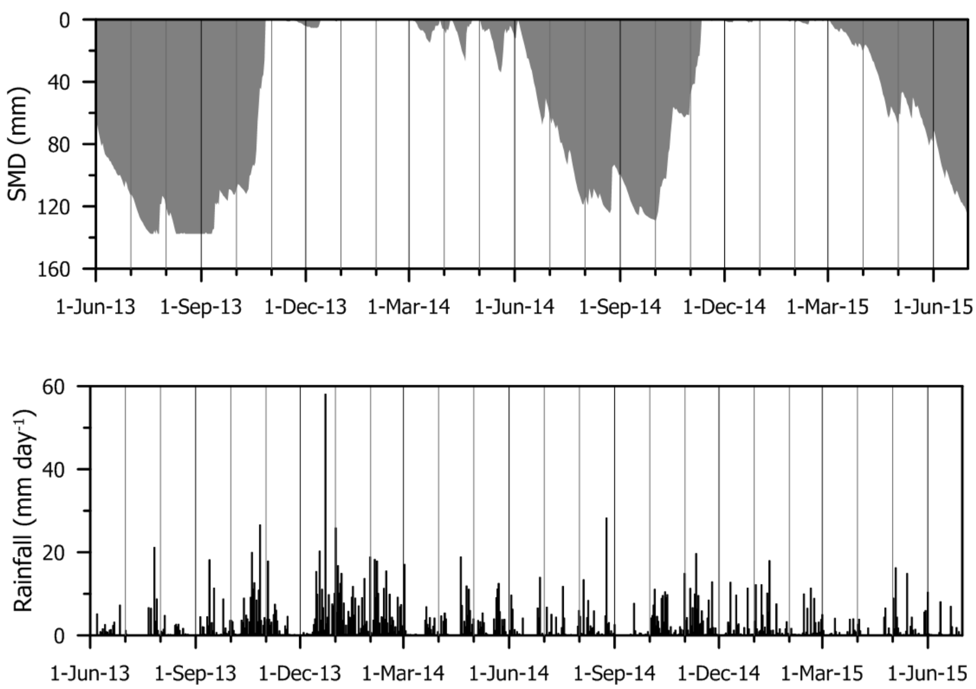

Figure 2. Soil Moisture Deficit (mm) and Daily Rainfall totals (mm) from June 2013 to June 2015.

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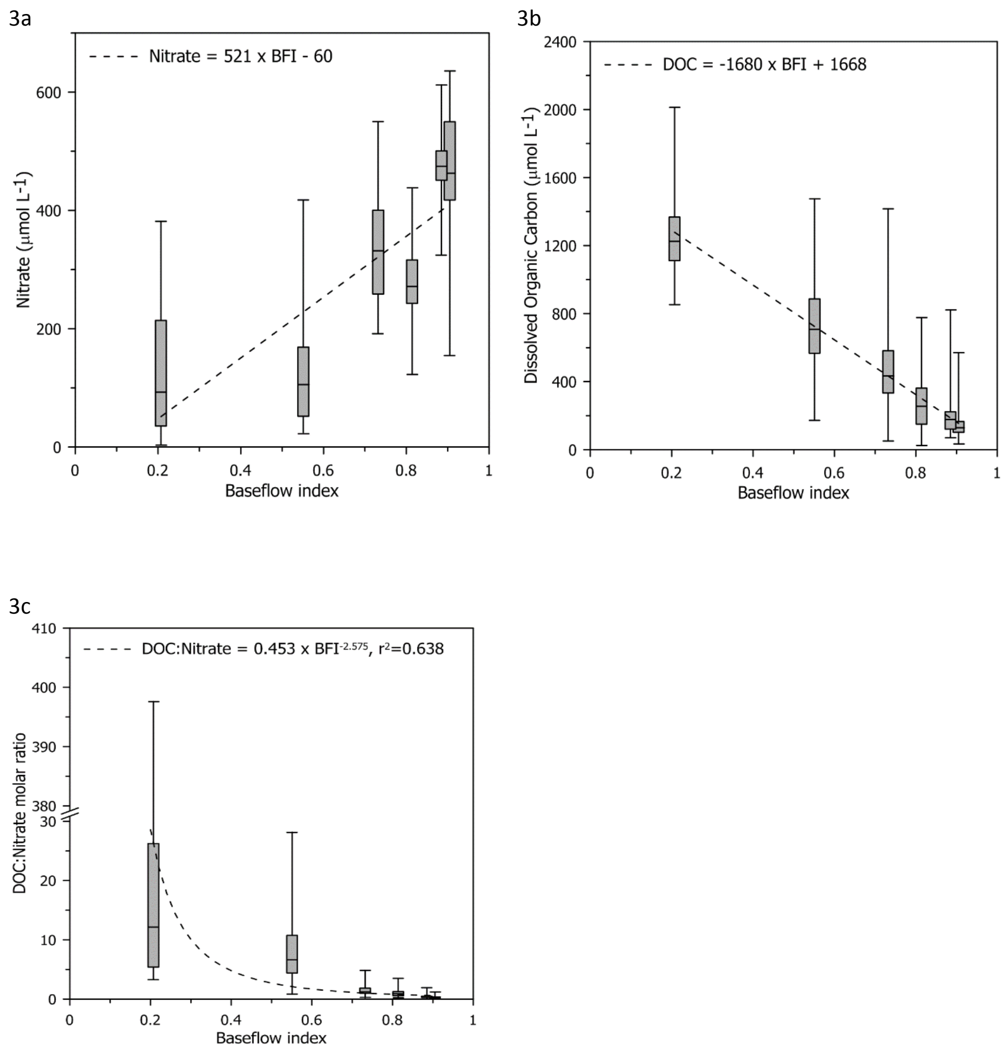

Figure 3. Relationship between (a) nitrate surface water concentration and baseflow index; (b) DOC surface water concentration and baseflow index; and (c) DOC:nitrate molar ratio and baseflow index for six sub-catchments in the Hampshire Avon.

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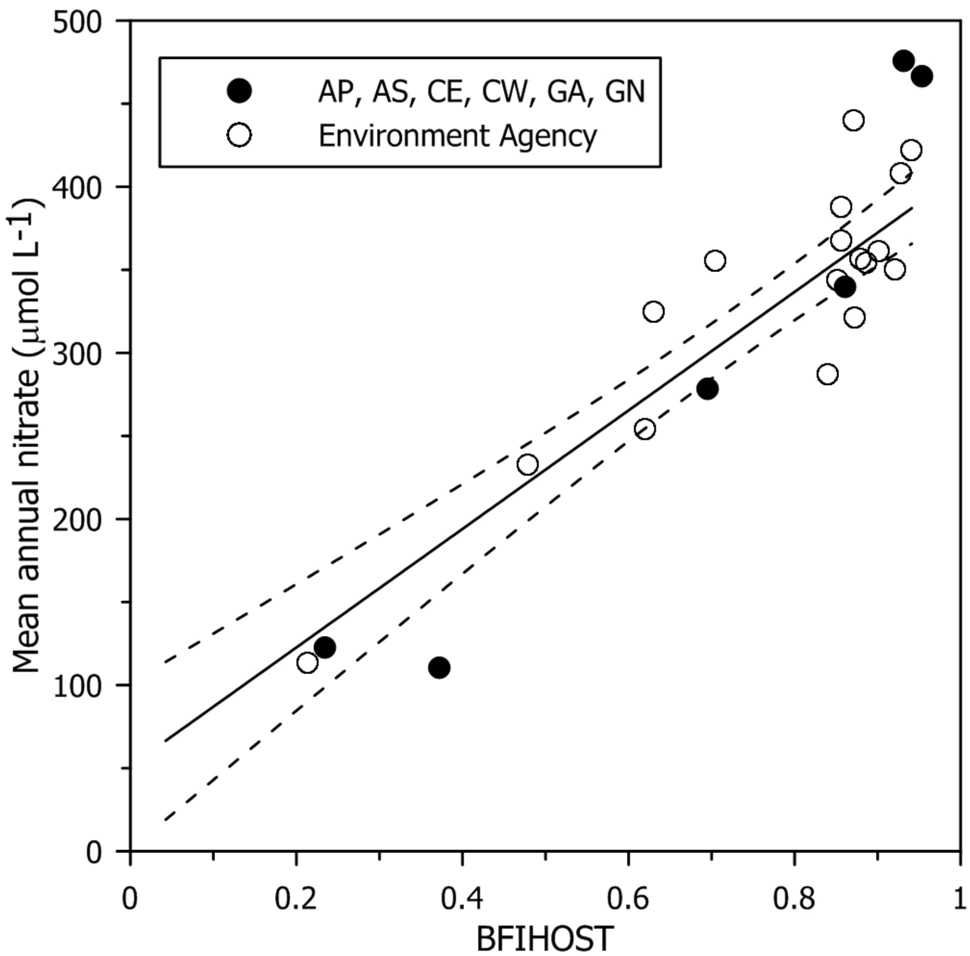
1104 

1105 Figure 4. Relationship between nitrate concentration and baseflow index for this
1106 study and Environment Agency Harmonised monitoring sites upstream of Salisbury
1107 in the Hampshire Avon (June 2013 - 2014).

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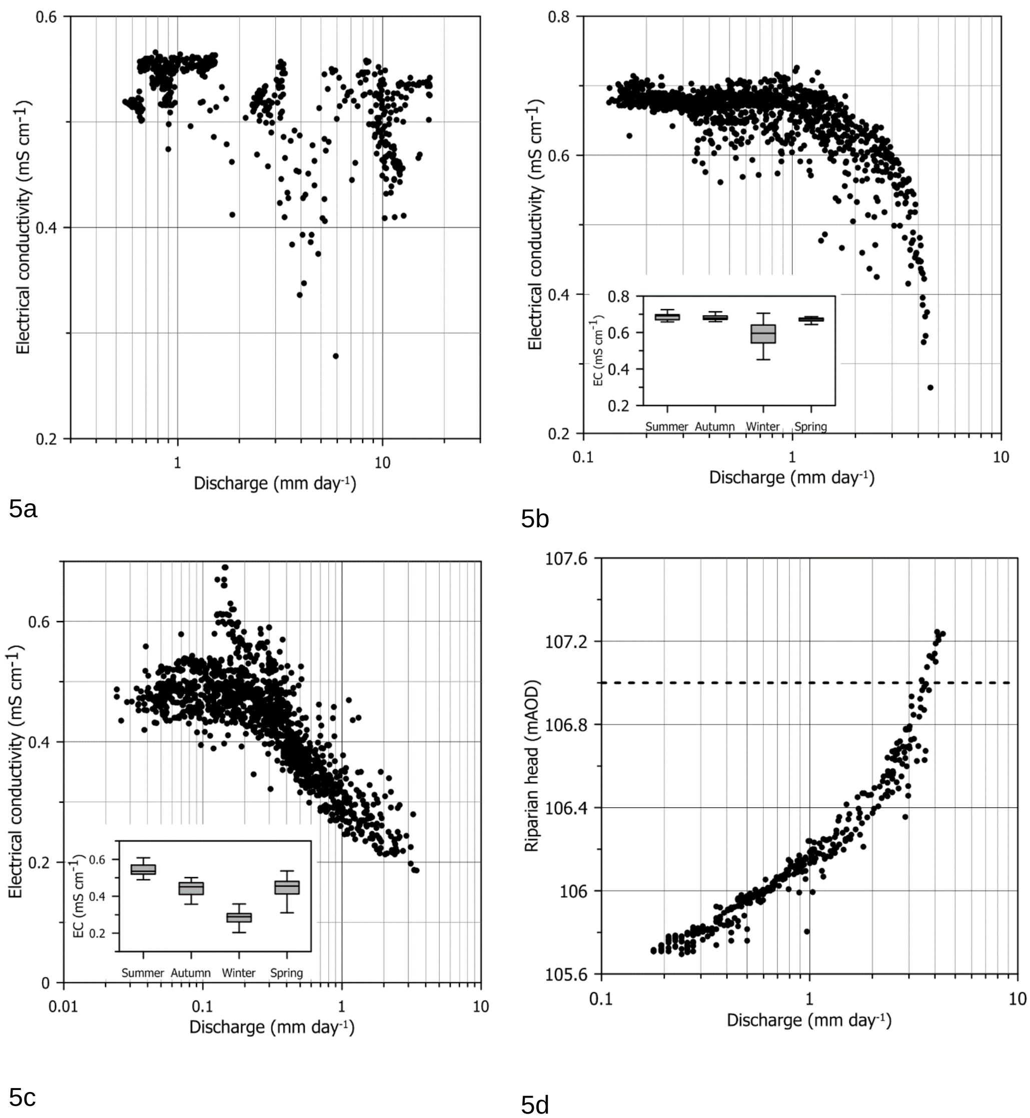

Figure 5. Relationship between Electrical Conductivity and Discharge for three sub-catchments of contrasting geology in the Hampshire Avon (a) Chalk - CE; (b) Greensand - GA; and (c) Clay – AS (June 2013 – 2015). Inset box-whisker plots indicate seasonal variations in electrical conductivity for Greensand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

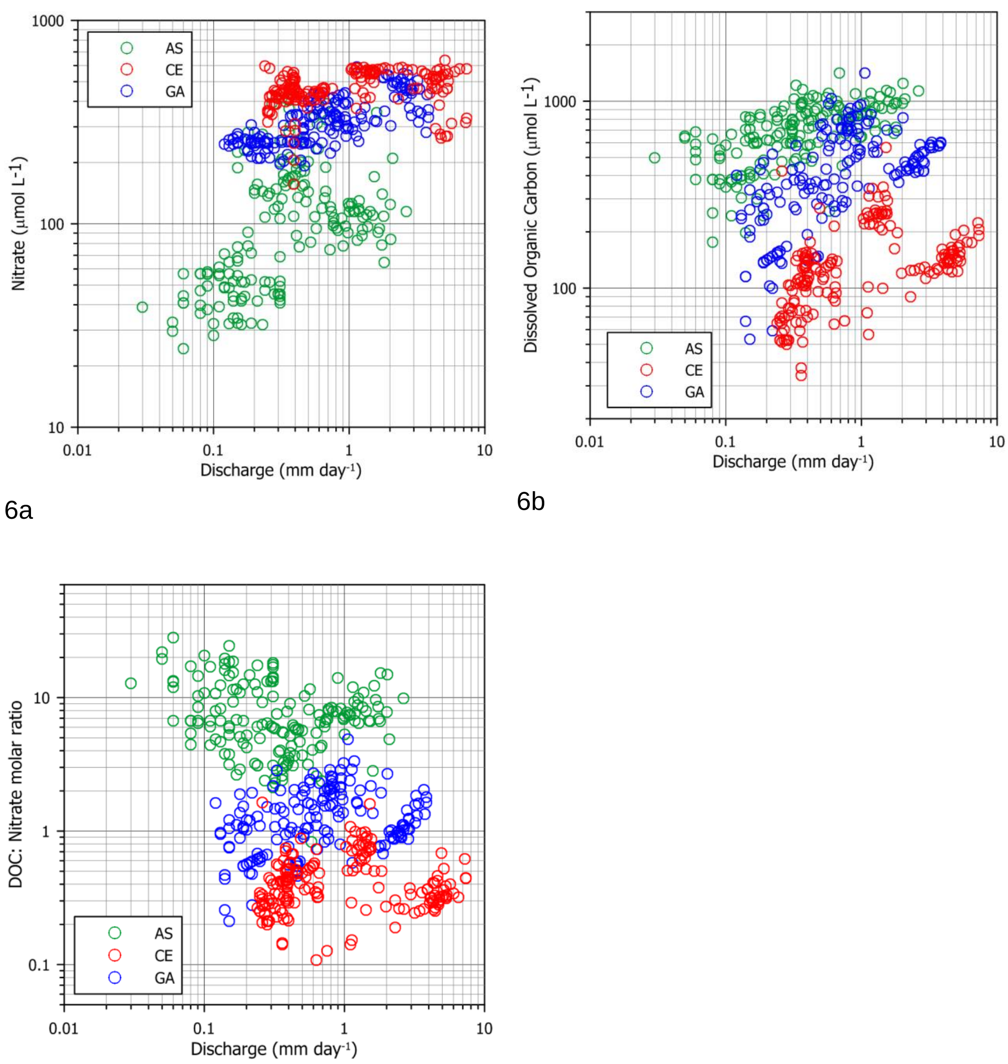

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Figure 6. Inter-site comparison of the relationship between (a) nitrate concentration and discharge; (b) DOC and discharge; and (c) DOC:nitrate molar ratio and discharge for three sub-catchments of contrasting geology in the Hampshire Avon: Chalk - CE; Greensand - GA; and Clay – AS (June 2013 – 2015).

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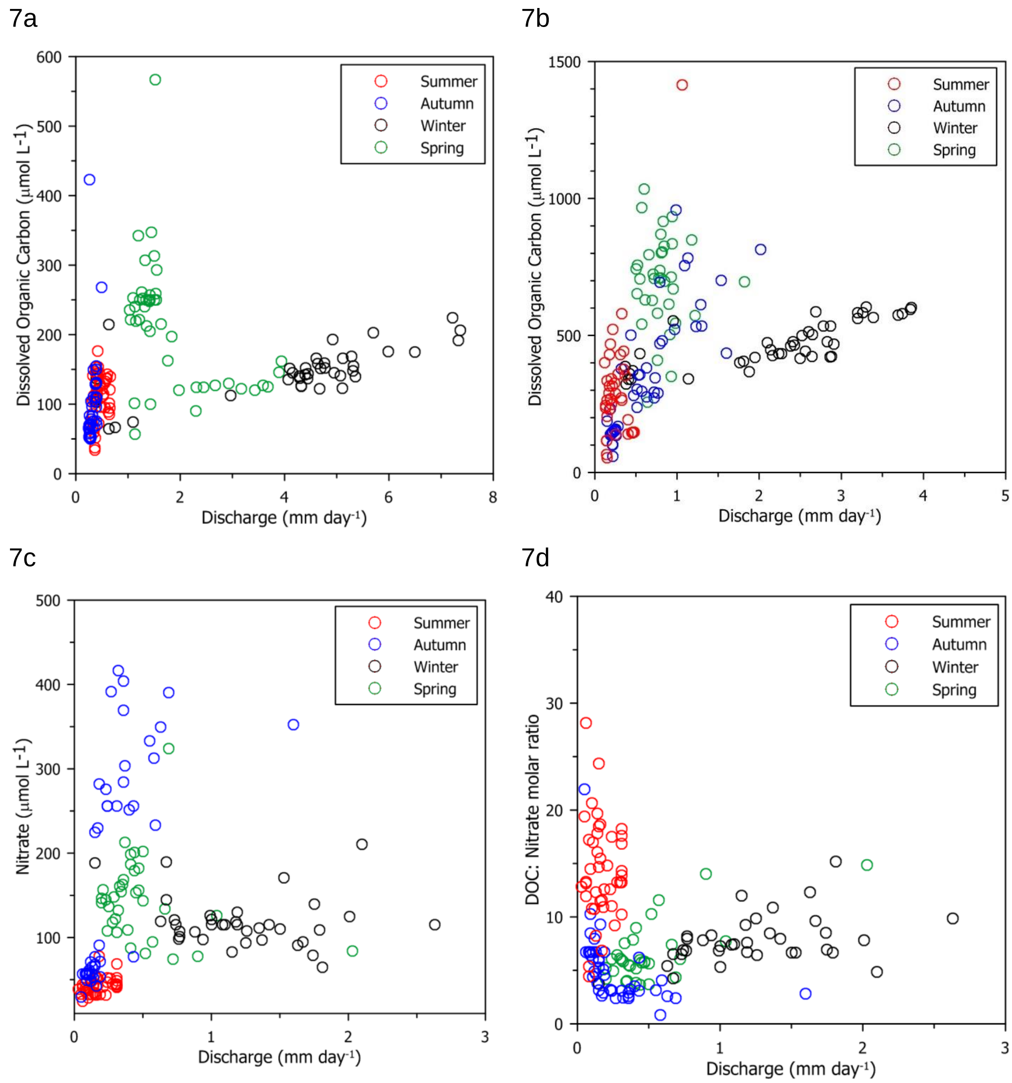

Figure 7. Seasonal variations in the relationship between solutes and discharge for three sub-catchments of contrasting geology in the Hampshire Avon. (a) Chalk – CE; (b) Greensand – GA; (c) Clay – AS (d) Clay – AS.