High-frequency monitoring of catchment nutrient response in the Demonstration Test Catchments to the end of the 2011-12 drought in England

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Abstract

Data from three distinct catchments in England equipped with bankside monitoring stations are presented as part of the UK Government funded Demonstration Test Catchments (DTC) project. The high-frequency bankside monitoring allows for simultaneous measurement of hydrology and hydrochemical parameters across different landscapes and geoclimatic

characteristics, with a range of differing flow behaviours, geochemistries and nutrient chemistries.

This paper brings together findings from all three DTC research groups to compare the hydrological and hydrochemical trends during the water year 2011-12, the beginning of which was unusually dry, with a sudden change to a wet summer. This transition period in April 2012 is examined in terms of the large flows experienced in each catchment as a result of a sudden increase in saturated conditions due to a large rainfall event that affected all three catchments, including the in-stream response of nitrate and phosphorus fractions (total phosphorus and total reactive phosphorus), measured at a half-hourly time step. This transition period provided insight into how the catchments behaved under relatively similar antecedent drought conditions. Both the year-long time-series data and the individual storm responses reveal different pollutant pressures and pathways operating at the three tributary sites. The collected data highlight the scale of the challenges faced by environmental managers when designing mitigation measures to reduce the flux of nutrients to UK river systems from diffuse agricultural sources and also in adapting to future extreme weather events under climate change.

Keywords: High-frequency monitoring, catchments, nitrogen, phosphorus, hysteresis, Demonstration Test Catchments

1. Introduction

The European Union Water Framework Directive (WFD) (European Parliament, 2000) is one of the most ambitious and encompassing pieces of water policy introduced on an international basis in recent years (Dworak et al., 2005; Johnes, 2007a; Liefferink et al., 2011) and aims to maintain and improve the quality of inland and coastal waterbodies, largely based on ecological rather than chemical status. It is well documented that, throughout Europe, nitrogen (N) and phosphorus (P) enrichment is contributing to the degradation of surface water and groundwater bodies resulting in non-compliance with legislation, albeit with different sources, mobilisation mechanisms, timescales of loss, transformations, attenuation pathways and types of ecological impact (Withers and Lord, 2002; Cherry et al., 2008; Billen, 2011; Grizzetti, 2011; Leip, 2011). The improved removal of nutrients at wastewater treatment plants is reducing point source inputs, meaning that non-point or diffuse sources are becoming relatively more important. Improved monitoring has been identified as integral to the success of the WFD (Dworak et al., 2005; Johnes, 2007b) and, therefore, requires a transition from conventional strategic monitoring networks to those that support a more integrated approach to water management (Collins et al., 2012). The current national water quality monitoring performed by the Environment Agency (EA) in England, despite the deployment of *in-situ* monitoring stations under the National Water Quality Instrumentation Service (NWQIS), largely consists of monthly spot sampling, particularly for the determination of nutrient chemistry. Such infrequent sampling has been widely documented as being inadequate for representative assessment of watercourse. Weekly sampling typically misses critical storm events, thereby undermining characterisation of the close coupling between hydrological and chemical dynamics, and resulting in erroneous estimation of concentrations and loads (Kirchner et al., 2004; Johnes, 2007b; Palmer-Felgate et al., 2008; Jordan and Cassidy, 2011; Wade et al., 2012). Even daily samples fail to represent the complexity of diurnal patterns of many hydrochemical determinands in catchments (Kirchner et al., 2004; Scholefield et al., 2005; Wade et al., 2012). Appropriate understanding of the relative contributions and timing of N and P inputs to rivers and streams is therefore of central importance for targeting mitigation options most effectively (Jarvie et al., 2010), meaning that higher temporal resolution water quality monitoring is central to the science that will allow achievement of WFD aims in respect of managing nutrient impacts in the freshwater environment (Jordan et al., 2005).

The greatest change in concentration and riverine transport of nutrients often happens during storm events (Evans and Johnes, 2004; Haygarth et al., 2005; Rozemeijer and Broers, 2007; Haygarth et al., 2012). Hysteresis patterns in concentration-discharge plots during periods of high flow, where the concentration of a determinand is different on the rising limb to the falling limb of the hydrograph, have frequently been used to infer sources and potential pathways of pollutants in catchments (Evans and Davies, 1998; House and Warwick, 1998; McKee et al., 2000; Bowes et al., 2005; Ide et al., 2008; Siwek et al., 2013). "Clockwise" loop trajectories represent a rapid delivery of the determinand from the source to the sampling point, indicating close proximity of the source in order to be transported so rapidly (Bowes et al., 2005). "Anticlockwise" trajectories are likely to be associated with slower subsurface pollutant pathways in the case of dissolved determinands (House and Warwick, 1998) and slow transport of bed-load, soil erosion from upper slopes or bank seepage for determinands more associated with particle-bound transport (Bowes et al., 2005).

Anticlockwise trajectories can also indicate the influence of point sources as dissolved and particulate nutrients continue to be transferred from areas of stored hydraulic head such as dairy shed retention ponds or septic tanks (McKee et al., 2000). Inferences of runoff based on concentration-discharge plots are strongest when additional information is available about prominent hydrograph components and when end member determinand concentrations are available (Chanat et al., 2002). However, such plots are simple to construct, the different shapes produced highlight the major processes determining pollutant transport, which can inform more intensive studies of end members and pathways using more involved techniques with isotopes and other geochemical tracers.

As part of the Demonstration Test Catchments (DTCs) programme in England, high temporal resolution monitoring equipment has been installed in three representative catchments (Figure 1) with different landscape characteristics and farming systems to assess whether new farming practices, which aim to reduce diffuse pollution from agriculture, can also deliver sustainable food production and environmental benefits (LWEC, 2013). Data collected in sub-catchments equipped with bankside monitoring of nitrate, total phosphorus (TP) and total reactive phosphorus (TRP) concentrations are being used to understand catchment dynamics during the first phase of research and detecting change in water quality at the sub-catchment scale after the implementation of a variety of different mitigation measures on participating farms during the second phase of research.

The aim of this paper is to examine the hydrological and chemical trends recorded in the three DTCs during the hydrological year 2011-12, including an in-depth examination of an unprecedented transition from drought stress to flood risk across much of England in April 2012. Rainfall, discharge, nitrate, TP and TRP data are examined from monitoring stations in targeted tributaries from each DTC catchment: the Wylye tributary in the Hampshire Avon; the Blackwater Drain tributary in the Wensum; and the Newby Beck tributary in the Eden. Antecedent conditions are examined together with hydrochemical trends in each tributary, and hysteresis loops and export rates have been constructed and calculated to examine the possible transport mechanisms occurring for each nutrient type at each site in response to the unusual meteorological conditions captured. Whilst the data presented from this period are only a snapshot of the intricate set of processes that are being pieced together to make up a more comprehensive picture of hydrological and hydrochemical functioning, they highlight the spectrum of catchment responses triggered by large storm events and, therefore, pressures acting in each DTC; thus demonstrating the value of a national research platform for understanding the responses of different catchment types.

2. Methodology

2.1 Site descriptions

The location of the three DTCs is shown in Figure 1 and Table 1 provides a summary of the main characteristics of each catchment. The Cretaceous Chalk, the UK's principal aquifer dominates the hydrogeology of the Avon catchment. The Hampshire Avon and its tributaries have a large component of groundwater in their flow with high base flow indices (>0.7) (Marsh and Hannaford, 2008). It has been recognized that the Upper Greensand also supports baseflow to rivers in the northern and western part of the Wessex Basin, including the Hampshire Avon (Soley et al., 2012). The River Wylye sub-catchment is underlain by chalk, with Upper Greensand in the west of the catchment. The Upper Greensand aquifer is underlain by Gault Clay providing an impermeable layer and means that the overlying shallow aquifers can be very productive (Allen, 2014). Farming systems in this sub-catchment tend to be intensive mixed arable and livestock production; fertiliser application rates on crops such as winter wheat are typically around 200 kg N ha^{-1}. The river experiences both nutrient and sediment pressures (Yates and Johnes, 2013).

As in the Hampshire Avon, the Chalk aquifer underlies the Wensum catchment. To the east of the catchment the Chalk is overlain by the Pleistocene Wroxham Crag Formation of sands and gravels. There exists a complex sequence of Quaternary strata over much of the catchment exhibiting glacial tills, sands, gravels, alluvium, peat and river terrace deposits. The presence of low permeability tills in excess of 15 m thickness in interfluve areas restricts infiltration to the underlying Chalk aquifer (Hiscock, 1993; Hiscock et al., 1996; Lewis, 2014). In the Blackwater sub-catchment, the western reach is underlain by glacial tills with clay-rich, seasonally wet soils developed on chalky boulder clay, whereas in the eastern reach the deposits comprise glacial sands and gravels with well drained sandy loam soils. The Blackwater sub-catchment is used for intensive arable production with nitrogen fertiliser application rates of around 220 kg N ha^{-1} on cereal crops. The tributary experiences pressures from both sediment and nutrient fluxes.

The Eden Valley in Cumbria is generally underlain by Permo-Triassic sandstone, which is classed as a Principal Aquifer. Approximately 20% of the sandstone that outcrops is free of superficial deposits. Superficial deposits cover the remaining 80% which consist of glacial tills and sands and river alluvium. Generally these superficial deposits are thin with thicknesses less than 2 m over 60% of the catchment but do exceed a thickness of 30 m to the west of Brough. Depth to groundwater is significant over much of the Eden catchment (Butcher et al., 2008). The Newby Beck tributary is underlain by low permeability glacial deposits over Carboniferous limestone and is a typical grassland catchment encompassing a mixture of dairy and beef production with associated livestock grazing pressures. Fertiliser application rates on grassland are in the region of 56 kg N ha^{-1} and 17 kg P ha^{-1}, whereas on arable land, rates are in the order of 127 kg N ha^{-1} with variable slurry applications for P and K. The harsher climate in the Eden catchment means there are fewer optimal days for cultivation so that seed beds are established in sub-optimal conditions. This often results in less vegetation cover and in some cases, no establishment at all, resulting in pollution pressures from sediment and P on receiving waters.

2.2 DTC monitoring infrastructure

Each DTC has a monitoring network installed in target sub-catchments equipped to measure multiple meteorological, hydrological, hydrogeological and hydrochemical parameters. Rainfall in the sub-catchments is monitored using tipping bucket rain gauges. At all monitoring sites, river discharge is gauged at 15- or 30-minute resolution. In the Wylye, discharge is measured at an adjacent EA flow monitoring station at Brixton Deverill. The monitoring points in the Blackwater and Newby Beck are equipped with pressure transducers in stilling wells to provide a fixed interval record of water level. Data collected from the pressure transducers are used in combination with regular flow gauging data to develop stage-discharge rating curves. Further data are being collected using *in situ* acoustic Doppler flow meters (Argonaut-SW, Sontek) in the Blackwater and Newby Beck to estimate discharge using velocity measured from two vertical acoustic beams, together with the stage and stream profile, the latter programmed at installation. Nutrient concentration data are collected at 30-minute temporal resolution using walk-in sampling stations located in each DTC. The stations are equipped with Hach Lange nutrient analysers with a flow-through cell housing a Nitratax Plus SC probe, which measures nitrate concentrations (as NO_3-N) via an optical sensor. A Phosphax Sigma draws samples from the flow-through cell via a Sigmatax

SC sampling and homogenisation unit to measure P (as TRP and TP), as documented elsewhere (Owen et al., 2012; Wade et al., 2012).

2.3 Quality Assurance procedures

The Hach Lange nitrate sensors are calibrated every three months using a standard solution. The Phosphax Sigma is automatically cleaned and calibrated daily using reagents that are replaced every three months. Additional cleaning of removable parts within the Sigmatax is carried out monthly, with pump tubing replaced every three months. Six-monthly services include optical probe calibration performed by a qualified Hach Lange engineer. This frequency of calibration is sufficient to minimise drift in the *in situ* measurements.

Regular maintenance activities are carried out at different frequencies across the three catchments but involve at least monthly cleaning of flow-through cells, clearing of in-channel vegetation and debris where stage is monitored and cleaning of rain gauges. All DTCs perform manual flow gauging during periods of high and low flows, which show good agreement with discharge produced by *in situ* flow meters. All field work and maintenance activities are entered into maintenance logs for each site, which are used during data quality assurance (QA) procedures.

Validation of high–frequency nutrient data is carried out using routine daily spot samples in the Wylye, weekly spot samples in the Blackwater and monthly spot samples in the Newby Beck. These samples are analysed in laboratories following standard methods. Inter-laboratory comparisons are used to check consistency in analytical procedures between catchments. A Pearson correlation has been used to assess the strength of relationship between laboratory data and the *in situ* equipment during the hydrological year 2011-12 (Table 2) where a positive residual represents an over estimation of nutrient concentration by the *in situ* equipment. The data presented in this paper are uncorrected against the laboratory data.

Identification of errors in all data sets is carried out for all three catchments. Errors flagged as critical include: periods of maintenance when the data may be unrepresentative; equipment and power failures; or data below limits of detection. Discharge data from the Blackwater presented here have been smoothed using a moving average window of five measurements. All data presented in this paper have been Quality Assured.

2.4 Antecedent Precipitation Index calculation

A simple Antecedent Precipitation Index (API) was calculated for the three tributaries to represent the antecedent moisture conditions throughout the hydrological year from October 2011 to September 2012. The API was calculated according to Saxton and Lenz (1967) using equation 1:

$$API_j = K(API_{j-1} + P_{j-1}) \quad (1)$$

where j is the number of days, P is the daily precipitation (mm day^{-1}) and K is a decay constant. The value of K varies seasonally reflecting evapotranspiration losses and is usually between 0.85 and 0.98. A fixed value of 0.9 was chosen for all three sites.

2.5 Hysteresis index calculation

The hysteretic behaviour of nitrate, TP and TRP, were investigated in each of the events in the Wylye, Blackwater and Newby Beck (Figures 5-7). To aid comparison between events and catchments, the hysteresis index, HI_{mid}, was calculated using the method outlined by Lawler et al. (2006). The mid-point discharge (Q_{mid}) was calculated and the nutrient parameter values were interpolated at the Q_{mid} for the rising (N_{RL}) and falling (N_{FL}) limbs. HI_{mid} was then calculated as follows: where $N_{RL} > N_{FL}$, $HI_{mid} = (N_{RL}/N_{FL})-1$, or where $N_{RL} < N_{FL}$, $HI_{mid} = (-1/(N_{RL}/N_{FL}))+1$. The index indicates whether the hysteresis is positive (i.e. clockwise) or negative (i.e. anticlockwise), and the larger the index, the greater the difference in concentration of the nutrient on the rising and falling limbs of the hydrograph (Table 5).

3. Results

3.1 Temporal hydrological and hydrochemical trends

Figure 2 shows the high-frequency time-series data for the three sites from October 2011 until September 2012 for nitrate, TP, discharge, rainfall and API for the Wylye, Blackwater and Newby Beck tributary sites of the three DTCs. The high-frequency nutrient monitoring in the Wylye did not commence until March 2012. There are step changes in the Wylye discharge data which are caused by the turning on and off of a groundwater borehole discharge point, operated by Wessex Water, as a method of stream support during dry periods.

A stream support time-series is shown in Figure 2. The discharge in the Wylye shows the strong influence of chalk groundwater in this baseflow dominated catchment, with relatively few individual discharge peaks relating to specific periods of rainfall, but long recessions after extended periods of rainfall when API values are high. The start of the hydrological year was very dry, with discharge increasing only at the end of April during the event studied here. Two periods of maximum discharge occurred in May, and then again in July to August. Nitrate consistently showed dilution of the baseflow contribution, which was around 7 mg N L^{-1} throughout the monitored period, in response to rainfall events. The nearest borehole to the sampling point was found to have a nitrate concentration of 6.9 mg N L^{-1}. The TP record shows that some large peaks occurred in the year, reaching 1 mg P L^{-1} during the event studied in detail here. Large peaks, however, appear to be relatively infrequent occurring only at times with high API values.

The Blackwater also experienced a dry winter in 2011-2012 but with the occurrence of some heavier rainfall in January and March. Despite the rainfall in January, discharge only responded with the onset of rainfall in March temporarily and then again in April and May for a more sustained period. The hydrograph shows long recession limbs due to the influence of groundwater, but to a lesser extent than in the Wylye. Nitrate concentrations in the Blackwater showed dilution patterns in the early part of the winter in response to rainfall in the catchment, but then from January onwards peaks in nitrate concentration beyond the baseflow concentrations were observed, reaching 14 mg N L^{-1}, although peaks were becoming less pronounced by August. There are large gaps in the TP record due to equipment failures. However, it is clear that TP responds quite rapidly to rainfall and increased discharge throughout the year, responding even to small events, although with much lower peak concentrations than in the Wylye and Newby Beck catchments.

In contrast to the Wylye and the Blackwater, the Newby Beck catchment experienced fairly typical winter rainfall at the end of 2011, but similar to the Wylye experienced unusually dry conditions for the early part of 2012 until the event in April studied here. The discharge record demonstrates the flashy nature of this tributary with very steep rising and falling limbs during individual storm events. The nitrate concentrations are much lower in Newby Beck than in the Wylye and Blackwater. However, similarly to the Blackwater, the Newby Beck exhibited dilutions of nitrate in response to rainfall at the end of 2011 but began to exhibit peaks during events from April until July, although reaching much lower peak concentrations than the Blackwater of around 6 mg N L^{-1}. TP concentrations in the Newby Beck respond very rapidly to rainfall, often exhibiting peaks of over 0.6 mg P L^{-1} throughout the year, apart from during the dry start to 2012.

3.2 Antecedent conditions and April storm response

Each DTC experienced higher than average rainfall in April, prior to a large storm which moved across the country between 25 and 29 April. The impact of this storm event was observed in all three of the DTCs and marked the transition between a period of dry weather during winter 2011-2012 and the wet spring and summer 2012. Table 3 summarises the rainfall characteristics in each DTC during this period. Both the Wylye and Blackwater experienced two hydrological events in response to this storm whereas the Newby Beck experienced only one event, on 25 April. The API values for the Wylye, Blackwater and Newby Beck sub-catchments before the commencement of the storm were 26, 30 and 10, respectively, showing that soils were already beginning to wet up in the Wylye and the Blackwater sub-catchments, while conditions in the Newby Beck sub-catchment were extremely dry prior to the storm event. API values increased to a maximum of 74, 44 and 20 in the Wylye, Blackwater and Newby Beck respectively during the period studied. The higher starting API and maximum rainfall totals resulted in the largest event API value in the Wylye, whereas the lowest starting API value and the lowest rainfall total in the Newby Beck explain the smallest of the maximum event API values of the three catchments.

To put these storms at the end of April in context, exceedance curves for a) flow, b) nitrate concentration and c) TP concentration for each of the monitoring sites were calculated using data from one hydrological year (Oct 2011-Sept 2012). These plots (Figure 3) show the conditions in each catchment prior to the hydrological response and at peak response during the events studied here. It should be noted that there are substantial gaps in the TP record for the Wylye and the Blackwater owing to equipment malfunction. The flow duration curve plot (Figure 3a) shows that prior to the onset of the first event in the Wylye, flow conditions were very low relative to the rest of the year (87.9% exceedance), highlighting the dry antecedent soil conditions. The first rainfall event caused a small hydrological response (18.2 % exceedance) but flows receded quickly before the second, more extreme event occurred (0.02% exceedance). The Blackwater, by contrast, was already exhibiting relatively high flows before the first event (5.9% exceedance), due to heavy rainfall at the end of March and continued wet conditions in April 2012. Hence, in this catchment, both events resulted in extreme high flows (0.04 and 0.9% exceedance, respectively). Newby Beck had a higher relative flow than the Wylye prior to the event (61% exceedance), but also achieved an extreme high flow at peak discharge (0.6% exceedance). Therefore, the rainfall considered in this storm event analysis resulted in extreme flows in all three DTCs, regardless of antecedent soil moisture conditions.

The nitrate exceedence curve (Figure 3b) shows that for the Wylye there was little variation in nitrate concentration for much of the year, with no high concentration extremes. However, both storms showed dilution of nitrate concentration during peak flows (6.3 mg N L^{-1} before the rainfall commenced), particularly for the second event, when one of the lowest concentrations of the year was detected (5.3 and 2.7 mg N L^{-1} and 97.6 and 99.6% exceedance, respectively). In contrast, nitrate concentrations in the Blackwater prior to both events were relatively high (6.5 and 7.0 mg N L^{-1} and 31.8 and 9.7% exceedance, respectively). The peak responses produced some of the highest nitrate concentrations detected in the hydrological year (13.5 and 11.6 mg N L^{-1} and 0.8 and 1% exceedance, respectively). There were no nitrate data for Newby Beck during this event as the nitrate sensor was not working.

In contrast to nitrate, TP underwent an extreme change from the beginning to the peak of the event in all three DTCs, with a pre-event concentration and exceedance of 0.1 mg P L^{-1} and 97.2%, respectively, in the Wylye; 0.03 mg P L^{-1} and 82.6%, respectively, in the Blackwater and 0.03 mg P L^{-1} and 92.7% respectively, in Newby Beck (Figure 3c). All three catchments exhibited high P concentrations during the peak of the first event with concentrations and exceedance of 0.89 mg P L^{-1} and 0.3% respectively, in the Wylye; 0.33 mg P L^{-1} and 0.4% respectively, in the Blackwater and 1 mg P L^{-1} and 0.003% respectively, in the Newby Beck. The second event in the Wylye achieved a similarly high concentration and exceedance (0.97 mg L^{-1} and 0.02%, respectively), whereas in the Blackwater the second event produced a lower concentration and exceedance (0.1 mg L^{-1} and 19.4%, respectively). These data demonstrate the significant effect of this extreme weather system on all three catchments in terms of runoff generation and the subsequent mobilisation of pollutants along a variety of flow pathways, when compared to conditions observed in each system over the remainder of the hydrological year.

3.3 Hydrograph response

The Wylye received a total of 88 mm of rainfall during the storm period studied, the highest of all the tributaries, which occurred on 25-26 April (45 mm) and 29 April (43 mm). This resulted in a small discharge response peaking at 0.3 $m^3 s^{-1}$ (<0.1 mm h^{-1}, 134% of pre-event discharge), followed by a second larger peak of 1.6 m^3s^{-1} on 29 April (0.1 mm h^{-1}, 361% of pre-event discharge, as shown in Figure 4a. In the Blackwater, the total rainfall between the 25 and 26 of April was 19 mm, which largely fell on the 25 April. This resulted in a maximum discharge of 1.4 m^3s^{-1} (0.3 mm h^{-1}, 699% of pre-event discharge), as shown in Figure 4b. This was followed by 20 mm of rain between 27 and 29 April, resulting in a second discharge peak on the 29 April with a maximum flow of 0.9 m^3s^{-1} (0.2 mm h^{-1}, 213% of pre-event discharge). Newby Beck received 32.3 mm between 25 – 27 April, with 79% of this rain falling on 26 April, and flows reaching 3.7 m^3s^{-1} (1 mm h^{-1}, 2425 % of pre-event discharge; Figure 4c). A small amount of rainfall was also recorded on 29 of April, but there was no significant response in river discharge.

3.4 Nutrient chemograph response

The chemographs for nitrate, TP and TRP during the event studied show very different responses between the Wylye, Blackwater and Newby Beck catchments (Figure 4). In the Wylye the stream nitrate concentration showed dilution with the onset of rainfall, the second event showing greater dilution than the first. In the Blackwater, by contrast, after a small initial dilution in nitrate, concentrations increased far above pre-event values, peaking after peak discharge, with a very long recession limb, the first event achieving a greater concentration maximum than the second. The chemograph for TP in the Wylye had a very steep rising limb and a much shallower falling limb, peaking at the same time as discharge in the first event but slightly after in the second event, yet achieving a higher concentration value. TP and TRP in the Blackwater showed a steep rising limb peaking before peak flow, with a similarly steep recession limb in the first event, and little response at all in the second. In Newby Beck the TP chemograph exhibited a double peak on the steep rising limb, peaking roughly at the same time as maximum discharge with a shallower falling limb. The TRP chemograph by contrast, had three small peaks, the largest of which occurred after maximum discharge, again with a longer recession limb.

N and P fluxes were also calculated for each rainfall event, along with total flow volumes (Table 4). For the purposes of this paper, load calculation did not include any estimation of the associated uncertainty. Nitrate-N exports were an order of magnitude higher in the Blackwater than the Wylye, with a loss of over a tonne in each event. The first event in the Blackwater had the highest load with an export yield to downstream reaches of 0.69 kg N ha^{-1}.

TP exports were more comparable between the three catchments, although exports were slightly higher in the Wylye and Newby Beck compared to the Blackwater and the highest export observed was from the second event in the Wylye. TRP exports were, again, comparable, with very similar export rates in the Blackwater and Newby Beck.

4. Discussion

4.1 Longer-term hydrological and hydrochemical dynamics

With high-frequency monitoring it is possible to infer a great deal about general influences on riverine water quality (Halliday et al., 2014). The discharge, nitrate and TP records from the monitoring stations from a complete water year reveal the complexity and breadth of nutrient dynamics and hydrological processes of three very different catchments. In the Wylye, the controlling influence on the in-stream nitrate dynamics throughout the monitored period was the nitrate-rich baseflow, the nitrate concentration in the chalk aquifer accounting for the steady concentration of nitrate in the channel, diluted at times of rainfall. The fact that there were no peaks in nitrate throughout the year reflects the permeable soils and the predominance of sub-surface movement of nitrogen to the chalk aquifer. The TP peaks detected in the monitoring period were of infrequent but high concentrations. The highest TP peaks occurred at the same time as the highest API values, representing the influence of surface flows during periods of high saturation in an otherwise sub-surface driven catchment. These findings accord well with results reported by Yates and Johnes (2013) in a wider study of nutrient hydrochemistry dynamics captured at daily sampling frequency at multiple sites in the Upper Wylye catchment.

In the Blackwater tributary, groundwater in the underlying chalk aquifer has very low nitrate concentrations (0.08 mg N L^{-1}) due to the restriction of recharge through the cover of low permeability clay loam soils developed on thick glacial deposits. The year-round baseflow nitrate concentration of around 4 mg N L^{-1} at the Park Farm monitoring point is most likely derived from the high nitrate input of the western tributaries in the catchment which have more impermeable clay soils receiving high nitrogen inputs from arable land, under-drained by a dense network of tile drains. Weekly sampling of drain discharge shows that nitrate concentrations are frequently between 3 and 20 mg N L^{-1}, with some of the deeper more continuously flowing drains having concentrations of around 10 mg N L^{-1} even in the summer months. The upward gradient of low-nitrate, deeper groundwater sources, through the more permeable glacial deposits upstream of the sampling point act to dilute this higher nitrate signal arriving from upstream. From October to December 2011, the dilution of stream nitrate with rainfall events occurred at times when the API values were low. From the end of January 2012 the nitrate concentration in the stream begin to exhibit peaks that exceed the baseflow concentration during the recession periods of individual storms, coinciding with higher API values. Greater levels of saturation in the catchment cause a greater number of tile drains to flow into tributary streams, with high nitrate inputs from mineral fertilisers and plant residues in the upper part of the catchment. The frequent occurrences of TP peaks even with small rainfall events show that P is easily mobilised. Sediment fingerprinting techniques carried out in the western part of the Blackwater suggest that clay-rich topsoils contribute proportionally more to the suspended particulate matter load measured in the stream at the beginning of storm events, whereas calcium-rich less weathered subsoils exposed in the eroded stream channel bank contribute proportionally more during the recession period (Cooper et al., 2013), the former likely to be rich in P due to the arable field origin.

The flashy nature of Newby Beck is attributed to the operation of rapid runoff response pathways (surface runoff and preferential flow in drains) and the lower baseflow index (Table 1). Although some groundwater connectivity is likely due to the shallow topsoil and the fact that in places the stream flows directly over the bedrock, groundwater contribution to streamflow is likely to be much less significant during stormflow than in the other catchments, particularly after a period of drought during which groundwater recharge might be expected. The very low nitrate concentrations under baseflow conditions are due to the lower inputs from nitrogen fertilisers, as arable farming only makes up a small proportion of the land use, and the lack of nitrate-rich baseflow contribution. The series of nitrate peaks observed between April and July 2012 are likely to reflect a combination of both incidental and/or preferential transfers of nitrate as a response to spreading of animal wastes and/or fertilisers, and the flushing out of nitrate accumulated in soil runoff pathways as a result of the winter drought period. The frequent and rapid response in TP concentration at the sampling point is attributed to rapid surface runoff generation exacerbated by extensive soil compaction from livestock trampling and silage production fields and transport of particulate P with eroded soil, with farm machinery tramlines also promoting high connectivity between sources and receiving waters. Tile drain flow is also likely to be a significant rapid response pathway once soils have reached field capacity.

The hydrochemical trends revealed by the bankside monitors are in agreement with the literature. Subsurface N transport dominates in catchments with permeable soils and geology, whereas near surface P transfer dominates in catchments with poor to moderately drained soils (Melland et al., 2008; Melland et al., 2012; Mellander et al., 2012). The importance of subsurface pathways are apparent in different ways in the Wylye and the Blackwater sub-catchments, with year-round elevated nitrate concentrations in the Wylye, diluted by periods of rainfall, and moderate year-round nitrate concentrations in the Blackwater with extremely elevated concentrations on the recession limbs of storm events spanning several days. Such long recession periods may become significant for the ecological status of receiving waters as they may persist into ecologically sensitive periods, such as summer low flows (Mellander et al., 2012). Therefore, in catchments dominated by subsurface flow, improving groundwater quality is essential in order to support good surface water quality (Rozemeijer and Broers, 2007) with mitigation strategies targeted at reducing leaching of nitrate (Di and Cameron, 2002). For catchments such as Newby Beck, where rapid flow response pathways dominate, mitigation measures are required that will attenuate these pathways (Wilkinson et al., 2010; Wilkinson et al., 2013), including reducing runoff and erosion on tracks and tramlines (Deasy et al., 2009a; Deasy et al., 2009b), trapping pollutants in edge-of-field areas (Deasy et al., 2010; Ockenden et al., 2012; Ockenden et al., 2014; Wilkinson et al., 2014) and also promoting strategies that aim to reduce soil compaction.

4.2 Short-term hysteretic behaviour

4.2.1 Nitrate

During the first rainfall event, nitrate showed anticlockwise hysteresis in both the Wylye and Blackwater, but produced very different shaped loops, with a more complex pattern arising in the Wylye. Although the overall shape of the first hysteresis loop in the Wylye was anticlockwise (Figure 5a), the loop starts in a clockwise direction, followed by a second small and third large anticlockwise trajectory before completion. The second event (Figure 5b) produced more of a figure-of-eight shaped loop in the Wylye, switching from anticlockwise to clockwise twice, and then remaining clockwise for the rest of the loop, hence the positive HI_{mid} value. These complicated patterns in the Wylye are due to the occurrence of several dilutions of the high nitrate concentration groundwater baseflow. Figure 2 shows that the API value was already reasonably high before this event, and that there had already been some more gradual dilutions in the baseflow nitrate concentration due to rainfall in the earlier part of April. Previous authors have shown that in Chalk catchments there exists a distribution of travel times for water moving through the landscape depending on the thickness of the unsaturated zone and the distance to the river, where rain falling on interfluves can take from several days to months to move from the surface to groundwater, whereas in parts of the catchment with thinner layers of unsaturated Chalk closer to the river there is mixing between old groundwater and modern water from recent recharge (Gooddy et al., 2006; Jackson et al., 2006). The multiple dilutions of the nitrate-rich baseflow of this river is therefore likely to be a result of the arrival of event water via multiple pathways with associated distributed travel times. The second event showed a similar pattern, although with fewer but more significant dilutions of nitrate and a longer recovery time to pre-event concentrations, hence the clockwise HI_{mid}. The highest API value for the entire year occurred during the second event coinciding with the substantial dilution in streamwater nitrate concentration. This type of anticlockwise hysteresis, where the loops start and end at the top-left of the plot, has been modelled by (Evans and Davies, 1998) who describe them as A3 loops, which are indicative of the mixing of two sources where the concentration of the determinand in pre-event water (groundwater contribution) is greater than in the event water (rainfall or surface water contribution).

The anticlockwise loops in the Blackwater indicated substantial transport of nitrate to the stream as opposed to the dilution of baseflow concentrations observed in the Wylye. For both events, the loops started and ended from the bottom left of the plot (Figure 5 c and d), as opposed to the top left of the plot for the Wylye. This was due to dilution with the onset of rainfall, followed by a subsequent increase beyond pre-event concentrations. The HI_{mid} value was higher for the first event than the second, but the fact that nitrate responded immediately to the second period of rainfall suggests that this source of N was not exhausted in the first event. Table 4 shows that the discharge of the second event was 72% of the first and that the N load of the second event was 74% of the first, which suggests that the amount of N transported to the sampling location was controlled by the volume of flow. Figure 2 shows the Blackwater experienced one large event in March and a smaller event at the beginning of April, both resulting in large nitrate peaks and that nitrate concentrations remained elevated at the start of the late April event. While the event studied in detail here was not the first to occur since the end of the drier than average winter period, there was still abundant nitrate in the catchment which had not been exhausted from earlier events. Other authors have found that shallow groundwater can contribute more nitrate to streamwater during the recession period of flood events, after the rise of the zone of saturation towards upper soil layers enriched by the accumulated nitrate pool (Rozemeijer and Broers, 2007; Oeurng et al., 2010), which could explain the mobilisation of nitrate during this particular event in the Blackwater. Soil water extracted at 90 cm depth from porous pots has revealed nitrate concentrations of up to 24.5 mg N L^{-1} in the clay loam soils under arable cultivation in the upper Blackwater. Soil nitrate would be easily mobilised by such events when there is connectivity of groundwater with upper soil layers via under-drainage. Anticlockwise hysteresis trajectories due to high concentration peaks during spring storm events in other catchments have been attributed to the dominance of the subsurface pathway during hydrograph recession combined with the timing of fertiliser application of winter wheat in January to April (Ferrant et al., 2013).

4.2.2 Phosphorus

The TP loop for the first event in the Wylye started in a clockwise direction, with TP peaking with peak flow, and then switching to an anticlockwise direction on the falling limb. In the second event in the Wylye, a figure-of-eight loop occurred again (Figure 6b), which was initially clockwise, becoming anticlockwise on the falling limb, which breached the 1 mg P L^{-1} limit fixed by the instrument at that time. The remobilisation of bed sediments deposited from the first event could account for the initial clockwise hysteretic behaviour (Eder et al., 2014), followed by the delayed delivery of the more distant component. Although there were no TRP data for this storm, other events from this site show that, even at peak flow, TP is dominated by TRP which can include dissolved forms as well as colloidal matter, which can be transported along rapid through-flow pathways in the saturated zone (Haygarth et al., 1997; Johnes and Hodgkinson, 1998; Heathwaite et al., 2005; Jarvie et al., 2008), possibly accounting for a large part of the TP signal. In addition, effluent containing TRP can be flushed under higher flows as shallow groundwater levels rise and intercept soakaways from small sewage treatment works and septic tanks (Jarvie et al., 2006; May et al., 2011; Yates and Johnes, 2013). The fact that TP concentrations in both events reached a concentration of at least 1 mg P L^{-1} suggests that TP was not exhausted from the first event, which had a smaller flow volume. The API value in the Wylye before the commencement of the storm was elevated from earlier rain in April, yet TP concentrations were fairly constant before this event with no sign of dilution, unlike nitrate (Figure 2). The lack of TP transport in March and April would suggest a build-up of P soil reserves. Other authors cite soil erosion on upper slopes, bank seepage and movement of coarse bed sediment and associated P-load for anticlockwise hysteresis in upland streams (Bowes et al., 2005).

In the Blackwater, TP responded immediately and peaked before the maximum discharge in both events (Figure 6c and d). In this case, the P was most likely to originate from topsoil (Cooper et al., 2013) remobilised bed-sediment (Ballantine et al., 2009), field drains and in-wash of P from the river banks (Laubel et al., 2000; Cooper et al., 2013) in response to rainfall and rising river levels (Bowes et al., 2005), while road runoff was also likely to be a source (Collins et al., 2010). Although both loops were clockwise, TP concentrations were lower in the second event, producing a substantially lower HI_{mid}. The similar amounts of rainfall and flow volumes generated in both events suggest that the source of TP started to show exhaustion in the Blackwater after two events in short succession. Figure 2 shows that there were several TP peaks as a result of events in March and early April. Mobilisation of P during these events could explain the rapid response in the event studied here as re-suspension of previously transported P, and would also explain why signs of exhaustion were evident by the second event. TRP behaved in a similar way to TP during both events in the Blackwater (Figure 7a and b), with clockwise hysteresis loops, indicative of flushing of a rapidly available source. There were also signs of exhaustion of this source as the second event showed a slower TRP response and a damped HI_{mid} (Bowes et al., 2005; Jordan et al., 2005; Jordan et al., 2007).The fact that TP and TRP fractions behaved similarly during both events, peaking before discharge, suggests that they were from a similar source and were mobilised along similar flow pathways as the event progressed in the catchment. The clockwise trajectories are in agreement with other studies of under-drained clay soils, attributed to the flushing of fine sediment particles from field drains during the rising limb (Djodjic et al., 2000).

In the Newby Beck, TP produced a very narrow but steep loop (Figure 6e). There were two peaks in the TP signal; an initial small peak at the beginning of the event, followed by a large peak coinciding with maximum discharge, which then quickly returned to pre-event concentrations, with the shape of the TP response mimicking the shape of the hydrograph (Figure 4c). This was reflected by the small clockwise trajectory at the beginning of the loop, followed by a second, larger clockwise trajectory for the remainder of the rising limb, switching to an anticlockwise trajectory on the falling limb, the steepness of the loop demonstrating the mirrored response of TP concentration to the hydrograph. In contrast, there were three TRP peaks, two small peaks occurring at the same time as the TP peaks and then a third, peaking after maximum discharge (Figure 9c). This resulted in two initial clockwise loops followed by a large anticlockwise loop on the falling limb, hence the negative HI_{mid} (Figure 7c). The fact that the TP and TRP responses were different indicates different sources or pathways of P in this sub-catchment. The first two peaks of both TP and TRP occurred at the same time as heavy rainfall, the first peak with around half the TP signal comprising TRP, the second with the peak largely consisting of particulate or unreactive fractions. This was reflected in both of the TP and TRP hysteresis loops, with the two initial clockwise trajectories on each, the difference being a much larger second clockwise trajectory on the TP loop. The third peak in TRP after peak discharge, when no significant rainfall occurred, produced the switch to the anticlockwise trajectory on the TRP loop, explaining the shift also seen on the falling limb to an anticlockwise trajectory on the TP loop. These patterns suggest that the first peak was a result of rapid mobilisation of a source of P close to the steam or in the stream itself that was equally composed of reactive and non-reactive forms of P, perhaps due to runoff from farmyards (Hively et al., 2005; Withers et al., 2009). The second peak was most likely the result of overland flow transporting largely particulate or unreactive P to the stream during the period of heavy rainfall, perhaps due to soil compaction through animal grazing and farm machinery traffic. Although TRP was present it comprises a much smaller part of the signal at this stage. The third peak in TRP could be explained by the sub-surface transport of dissolved and potentially colloidal P which has a delay in reaching the stream, presumably as the catchment wetted up and slower sub-pathways were activated. The API before the start of this event was low due to low rainfall in preceding months, representing the dry soils. The disproportionately large TP peak produced from the flow generated reflects the lack of exhaustion from previous events, unlike in the Blackwater. This agrees with the findings of Ide et al. (2008) that the mobility of particulate P increases as soil conditions become drier and Stutter et al. (2008) that steeper gradient headwater streams are high energy systems which quickly mobilise P during times of rainfall.

4.3 Relationships between water quality and meteorological conditions

There is no close modern parallel in the UK to the hydrometeorological conditions experienced over the first half of 2012, with widespread drought at the beginning of the year followed by sudden drought recovery beginning in late spring and early summer when evaporation rates normally exceed rainfall (CEH, 2012b). The rainfall from April-June in

England was nearly three times that of the preceding three months, which has not been experienced in over one hundred years (CEH, 2012b). The effects of other national droughts on water quality in the UK have been documented, such as the drought of 1976, which mainly focused on nitrate flushing with the onset of autumn rainfall (Foster and Walling, 1978; Burt et al., 1988; Jose, 1989). The effects of localised drought on P losses from UK catchments have been less well documented although authors previously have recorded that catchment P retention increased in a small groundwater fed catchment in the east of England over a four year drought period between 1988 and 1992 (Boar et al., 1995) and that the highest particulate P fractions recorded in a lowland river in the south of England during a three year period were in autumn 1997 after a prolonged drought period (Jarvie et al., 2002).

All three DTCs encountered higher than average rainfall in April 2012, but with discharges making slow recoveries from the dry conditions in March. Although the API values show that the three catchments were not experiencing identical conditions prior to the onset of the storm event that affected the whole country on the 25 April, the catchments were experiencing similar conditions due to a widespread national drought. The high-frequency monitoring captured this late April event, which marked the transition from a dry winter to a wet summer in all three catchments, allowing for the evaluation of responses to the connectivity of pollutant transfer pathways from previously dry soils in three different geographical areas. The extreme flows, along with nitrate and P concentrations achieved during the events as shown in the exceedance curves (Figure 3), demonstrate the impact of these unusual weather patterns within the context of one hydrological year. In the Blackwater, the most marked response was that of nitrate, exhibiting fluxes per hectare an order of magnitude higher than those seen in the Wylye. The spring of 2011 was exceptionally dry in the east of England, meaning that the movement of applied mineral fertilisers from the soil surface to the root zone of crops would have been limited, leading to a reduction in crop uptake at the time of fastest growth. A large pool of mineral N is likely to have accumulated in the soil, not only from fertiliser applications in the spring of 2011 and 2012, but also because prolonged drought conditions promote mineralisation of soil organic matter, resulting in large inputs to the stream when heavy rainfall did occur in March and April 2012. All three catchments exhibited large transfers of P, with comparable losses per hectare for TP, although slightly higher values were evident for the Wylye and Newby Beck. The first event in the Wylye, although smaller in a hydrological context, still resulted in a high maximum TP concentration, likely to consist largely of dissolved and colloidal forms of P, demonstrating the availability of P in the catchment prior to the event, while the second, larger event showed little sign of source exhaustion. The disproportionate P peak in response to discharge in the Newby Beck that was largely composed of particulate P has implications for management of soil erosion and sediment delivery to the River Eden, and gives clear guidance on the necessary focus for any such mitigation measures to reduce agricultural P loss to waters.

The common response observed across the contrasting conditions of the three systems studied points to the size of the nutrient pools stored in these catchments, where the pressures highlighted from this event appear to be from nitrate in the Blackwater, TRP in the Wylye and particulate P, and therefore sediment, in Newby Beck. Understanding the impact of meteorological conditions on catchment water resources and nutrient export are crucial, particularly when changeable weather conditions are occurring. In the two years of operating the high temporal resolution monitoring infrastructure in the DTC catchments, two extremes have been observed with 2011 being exceptionally dry and 2012 being extraordinarily wet. These pressures indicate the scale of the challenges faced by environmental managers when designing mitigation measures to reduce the flux of nutrients to UK river systems from diffuse agricultural sources in their catchments. Future mitigation options available to land managers need to reflect the heterogeneity of pollutant pressures and pathways acting across different landscapes and land uses with varying antecedent conditions.

4.4 The benefits of high-frequency water quality monitoring

The potential benefits of bank-side nutrient analysers have been widely discussed (Jordan et al., 2005; Jordan et al., 2007; Palmer-Felgate et al., 2008; Wade et al., 2012). The DTC project has been implemented by the UK Government as a long-term research platform. The high-frequency hydrological and hydrochemical monitoring enables continuous characterisation of three very different English catchments, with no bias towards particular flow regimes or sampling strategies. This allows extreme events such as recorded here to be put in the context of a data-rich time series, for example, a complete hydrological year. Storms are understood to be the major vehicle for pollutant transfer in catchments, particularly for particulate forms (Evans and Johnes, 2004; Haygarth et al., 2005; Jordan et al., 2007). Equally, high temporal resolution monitoring during baseflow periods provides insights into fine-scale patterns which highlight new avenues for research on catchment nutrient transfer processes, such as the significance of chronic P transfers on the eutrophic state of streams during low flows (Jordan et al., 2005). Here we have illustrated the benefits of calculating loads and the use of simple hysteresis plots to interpret the range of responses exhibited by the three DTCs to a particular storm event.

An on-going area of research in the wider scientific community is the determination of riverine nutrient loads using concentration-discharge relationships where discrete concentration samples are used with higher frequency flow measurements. However, hysteresis is usually not taken into account in load estimation techniques (Eder et al., 2010). The hysteresis loops constructed for the three catchments during the period studied here reveal different behaviours between catchments and between events within the same catchment. The hydrological response of any given catchment is a result of the interactions of numerous landscape properties (e.g. vegetation, topography, soil properties) and hydrometeorological inputs (rainfall, radiation), where the magnitude of interactions makes it difficult to identify dominant controls on water response (Woods and Sivapalan, 1999), and where heterogeneity exists at every scale (McDonnell et al., 2007). Water residence time dictates that contact time of water with sub-surface materials has a direct control on chemical composition and biogeochemical processing in hydrological units (McGuire et al., 2005). However, understanding where water goes when it rains, how long it resides in a catchment, which paths it follows (McGlynn et al., 2003) and which accumulated nutrient stores it interacts with and flushes to the channel is still a research challenge, which is difficult to quantify and conceptualise (Weiler et al., 2003). In addition, there is the complex biogeochemical processing that can take place in groundwater, the river corridor and in-stream, further complicating interpretation, not to mention the uncertainties involved in making quantitative measurements of rainfall, flow and contaminant concentration, and the resultant propagation of uncertainty when transforming measurements (McMillan et al., 2012). All of these factors vary in time, space and across seasons which is often the reason why model predictions of nutrients, even when quantifying the prediction uncertainties, fail to estimate fully the observed behaviour (Dean et al., 2009). Load estimations have been improved by accounting for hysteresis (Drewry et al., 2009; Eder et al., 2010), by using iterative parameter fitting techniques (Moliere et al., 2004) and creating individual models according to season, hydrograph limb and flow for long-term datasets (O'Connor et al., 2011). Even a small amount of carefully monitored high-frequency water quality data can be valuable in increasing understanding of concentrations, flow and catchment-scale processes (Drewry et al., 2009).

5. Conclusions

The data produced from high-frequency water quality monitoring infrastructure installed as part of the DTC project have provided in-depth information about the hydrochemical behaviour of three different catchments. The benefit of data obtained from such long-term monitoring infrastructure is the ability to investigate relationships between the range of potential environmental influences on water quality, such as the influence of meteorological conditions, as discussed here, or land use change, to be explored in the second phase of the DTC project. Hysteresis loops are simple to construct from high-frequency chemistry and discharge data, form a good basis for further research into catchment processes and also highlight the reality of the complex relationship between discharge, concentration and load estimation, where high-frequency data, such as those demonstrated here, are essential for improving understanding. The spectrum of pollution pressures highlighted by the DTCs represents the continuing challenge for environmental managers in mitigating against agricultural pollution and also in responding to climate change in the 21st century. The Fifth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC, 2013) recognises that the frequency of droughts and floods will increase as a result of anthropogenic greenhouse gas emissions. In addressing this global environmental challenge, the knowledge gained by high-frequency monitoring in the DTC catchments to the end of the 2011-12 drought in England provides insight into the types of processes likely to control nutrient fluxes during future extreme weather events. As highlighted by Whitehead and Crossman (2012), emerging research initiatives in the UK and elsewhere are now beginning to address water quality issues and climate change through integrated understanding of catchment processes and nutrient cycling to inform policy implementation and adaptation responses.

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Table 1. Summary characteristics for the Hampshire Avon, Wensum and Eden DTC tributary sites.

[a] From (Robson and Reed, 1999). [b] According to National Soil Research Institute classification.

BNG – British National Grid. m ASL – metres above sea level.

	Hampshire Avon	Wensum	Eden
Sub-catchment	Wylye at Brixton Deverill	Blackwater Drain at Park Farm	Newby Beck at Newby
Sampling location (BNG)	ST 868 401	TG 125 246	NY 600 213
Size of catchment (km^2)	50.2	19.7	12.5
Elevation of sampling point (m ASL)	189[a]	43[a]	233[a]
Aspect (° from north)	106[a]	144[a]	28[a]
Soils[b]	Sandy loam and silty clay loam soils from Ardington, Blewbury, Coombe and Icknield soil series	Chalky boulder clay and sandy loam soils from Beccles 1, Burlingham 1 and Wick 2 and 3 series	Clay loam and sandy clay loam soils from Brickfield, Waltham and Clifton series
Geology	Cretaceous Chalk and Upper Greensand	Quaternary glacial till, sands and gravels over Pleistocene Crag and Cretaceous Chalk	Glacial till over Carboniferous limestone
Annual average rainfall (mm)	886-909[a]	655[a]	1167[a]
Baseflow index (BFI)	0.93[a]	0.80[a]	0.39[a]
Landuse	Livestock and cereals	Arable crops	Livestock

Table 2. Relationship between laboratory samples and samples collected using bankside analysers using a Pearson correlation for each of the DTC tributary sites.

	Blackwater			**Wylye**		**Newby Beck**		
	TP (mg P L^{-1})	TRP (mg P L^{-1})	NO_3-N (mg N L^{-1})	TP (mg P L^{-1})	NO_3-N (mg N L^{-1})	TP (mg P L^{-1})	TRP (mg P L^{-1})	NO_3-N (mg N L^{-1})
Pearson correlation coefficient	0.86	0.81	0.91	0.87	0.87	0.97	0.86	0.45
p value	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mean of residuals	0.01	0.00	0.05	-0.04	-0.31	0.00	0.00	0.13
Standard deviation of residuals	0.01	0.01	0.42	0.07	0.38	0.03	0.03	0.60

Table 3. Storm event rainfall characteristics in each tributary.

*Data not available in the Wylye during the storm event.

	Wylye		**Blackwater**		**Newby Beck**
	Event 1	Event 2	Event 1	Event 2	Event 1
Date (2012)	25-26 April	29 April	25-26 April	27-29 April	26-27 April
Total rainfall (mm)	45	43	19	20	32
Max intensity (mm h^{-1})	*	*	5	1.8	4.1

Table 4. Nutrient fluxes for each storm event in the Wylye, Blackwater and Newby Beck as absolute load and export.

DTC tributary	**Event**	**Total flow volume**	**NO_3-N**		**TP**		**TRP**	
		(m^3)	**Load**	**Export**	**Load**	**Export**	**Load**	**Export**
		(mm)	**(kg N)**	**(kg N ha^{-1})**	**(kg P)**	**(kg P ha^{-1})**	**(kg P)**	**(kg P ha^{-1})**
Wylye	1	24437	90	0.018	13	0.003	--	--
		0.44						
	2	90275	359	0.075	56	0.011	--	--
		1.6						
Blackwater	1	134430	1364	0.692	14	0.007	8	0.004
		6.8						
	2	96506	1005	0.510	6	0.003	4	0.002
		4.9						
Newby Beck	1	230846	--	--	13	0.009	5	0.004
		16.5						

Table 5. Summary of estimated values of the hysteresis index, HI_{mid}, for each nutrient peak in the Wylye, Blackwater and Newby Beck.

DTC	Event	NO_3-N	TP	TRP
Wylye	1	-0.18	-3.16	--
	2	0.11	0.19	--
Blackwater	1	-1.08	2.25	2.4
	2	-0.43	0.48	0.63
Newby Beck	1	--	-0.02	-0.82

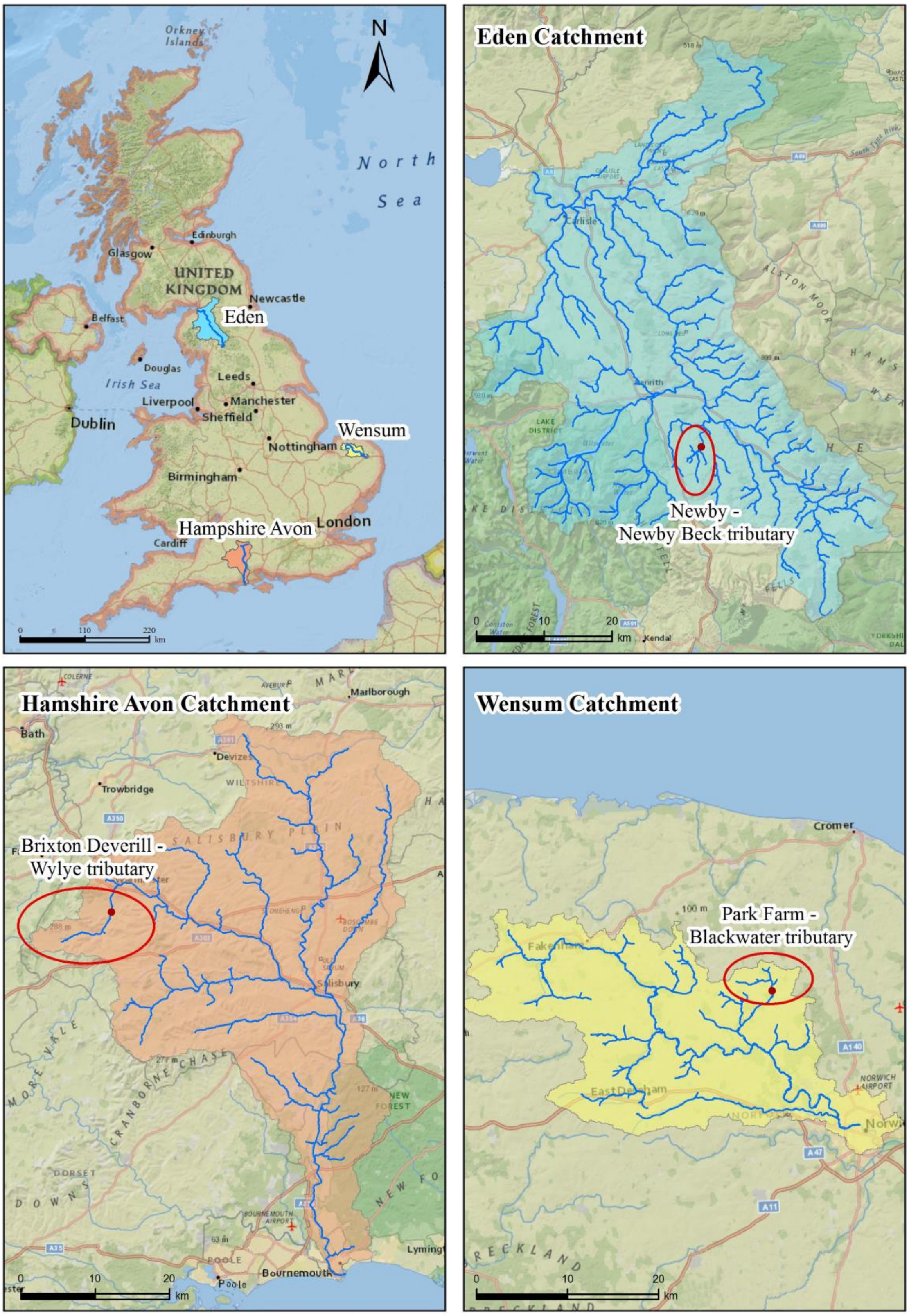


Figure 1. Location map of the UK showing the three Demonstration Test Catchments, the Hampshire Avon, Wensum and Eden; and the respective tributaries in each catchment, the

Wylye, Blackwater and Newby Beck. The red dot indicates the location of the bankside monitoring stations in the tributary sub-catchments. Sources: National Geographic, Esri, DeLorme, NAVTEQ, UNEP-WCMC, USGS, NASA, ESA, METI, NRCAN, GEBCO, NOAA, iPC.

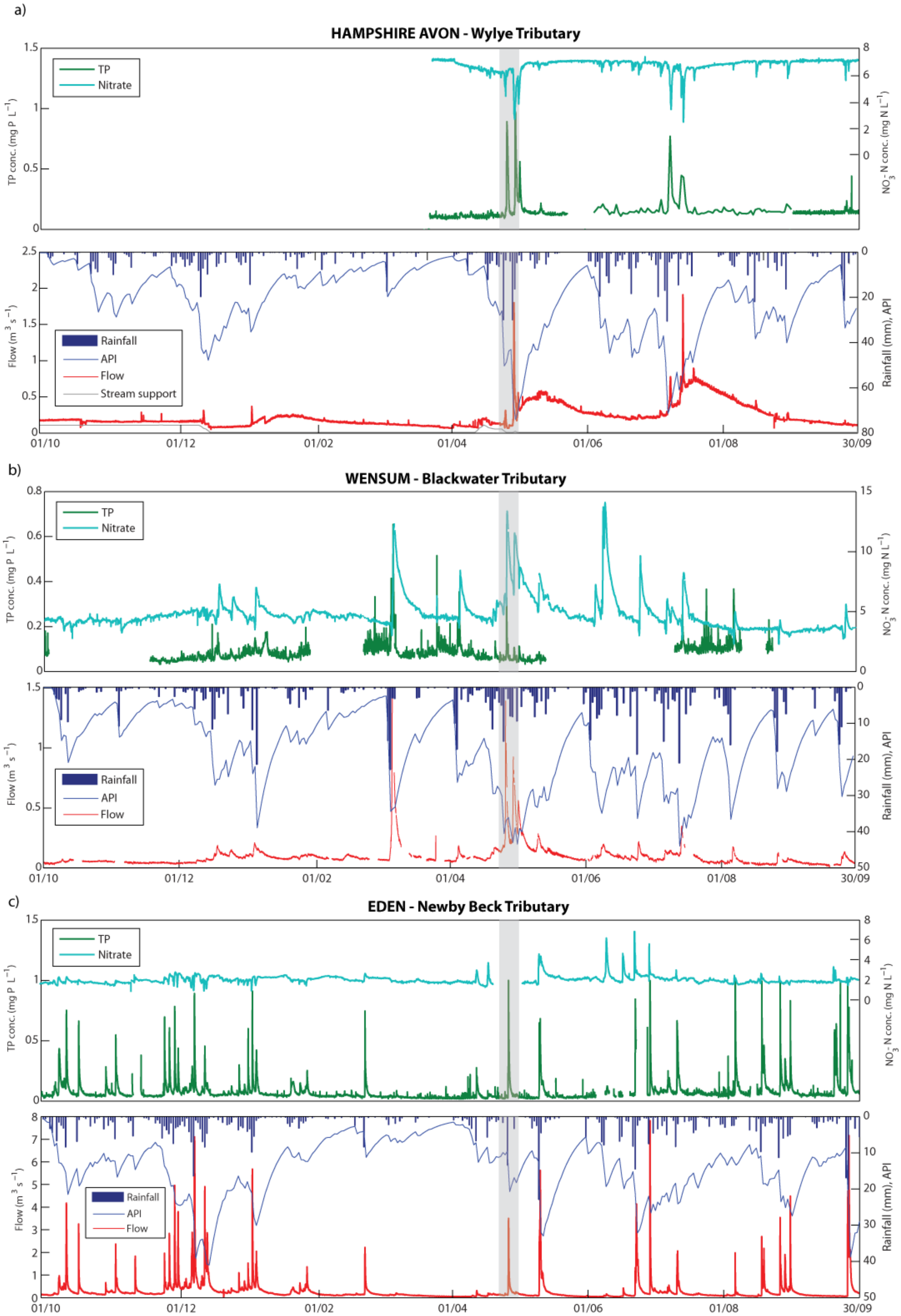
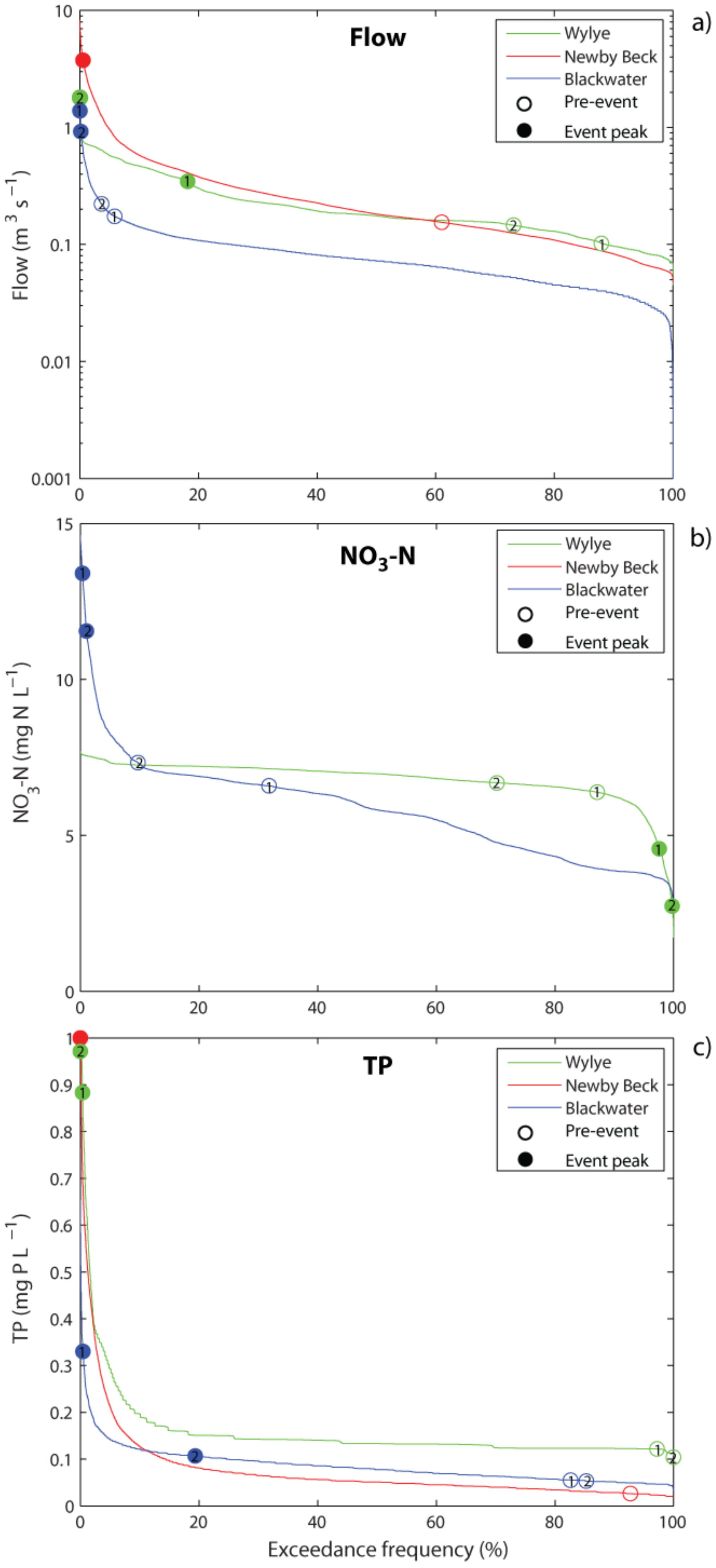

a)
HAMPSHIRE AVON - Wylye Tributary
TP
Nitrate
TP conc. (mg P L⁻¹)
NO₃⁻-N conc. (mg N L⁻¹)
Rainfall
API
Flow
Stream support
Flow (m³ s⁻¹)
Rainfall (mm), API
01/10
01/12
01/02
01/04
01/06
01/08
30/09
b)
WENSUM - Blackwater Tributary
TP
Nitrate
TP conc. (mg P L⁻¹)
NO₃⁻-N conc. (mg N L⁻¹)
Rainfall
API
Flow
Flow (m³ s⁻¹)
Rainfall (mm), API
01/10
01/12
01/02
01/04
01/06
01/08
30/09
c)
EDEN - Newby Beck Tributary
TP
Nitrate
TP conc. (mg P L⁻¹)
NO₃⁻-N conc. (mg N L⁻¹)
Rainfall
API
Flow
Flow (m³ s⁻¹)
Rainfall (mm), API
01/10
01/12
01/02
01/04
01/06
01/08
30/09

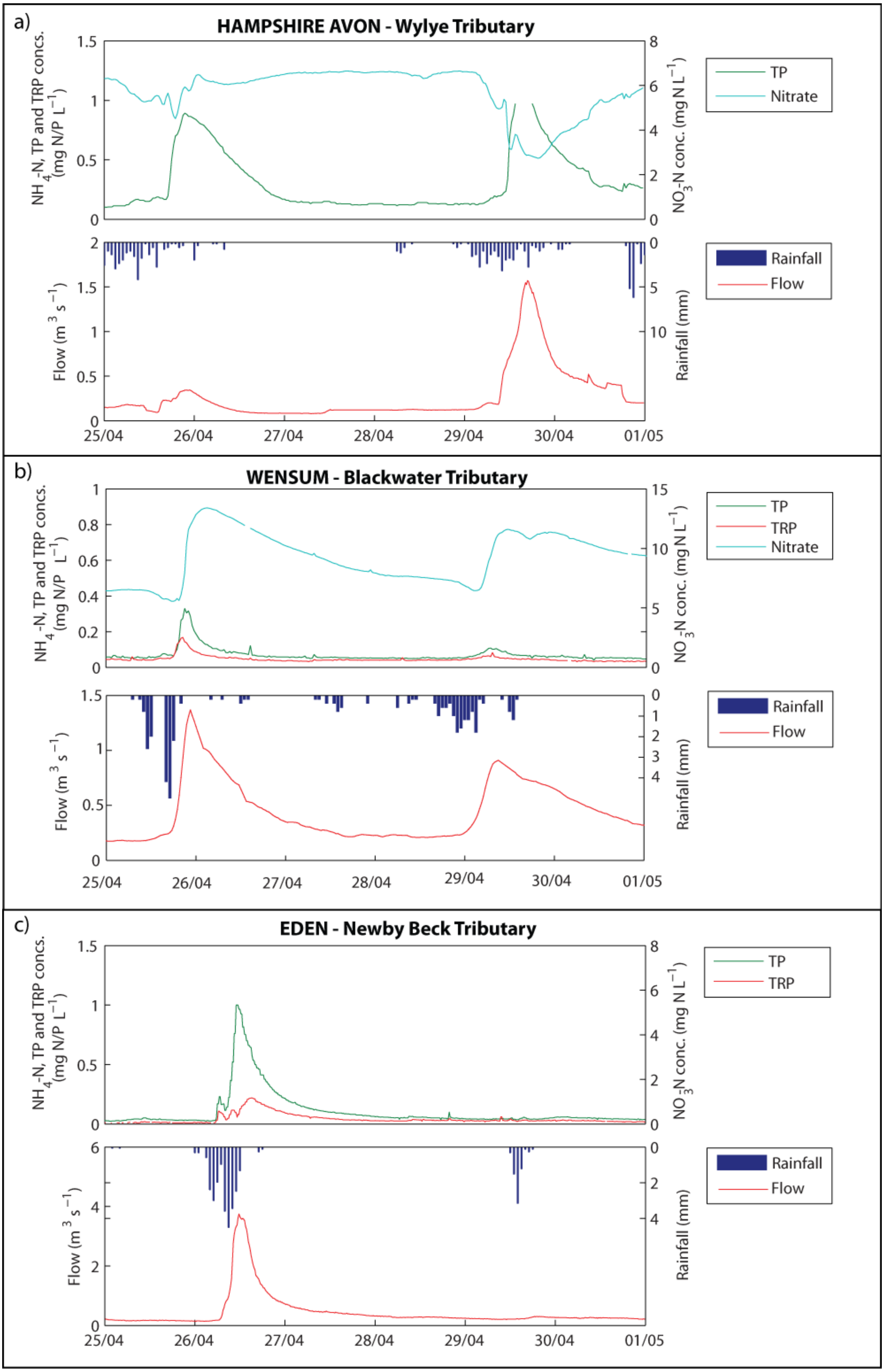
Figure 2. Plots showing rainfall, discharge, API, nitrate and TP for the hydrological year 2011-12 for: (a) Hampshire Avon Wylye tributary; (b) Wensum Blackwater tributary; and (c) Eden Newby Beck tributary. The shaded area indicates the storm event between 25 and 29 April 2012 examined in this paper. The operation of groundwater pumping for stream support is shown for the Wylye (see further explanation in Section 3.1).



Flow
a)
Wylye
Newby Beck
Blackwater
Pre-event
Event peak
Flow (m 3 s −1)
10
1
0.1
0.01
0.001
0
20
40
60
80
100
NO3-N
b)
NO3-N (mg N L−1)
15
10
5
0
TP
c)
TP (mg P L −1)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
Exceedance frequency (%)

24

Figure 3. Exceedance plots for: (a) flow; (b) nitrate; and (c) TP in the Hampshire Avon Wylye tributary, Wensum Blackwater tributary and Eden Newby Beck tributary. Open circles illustrate pre-event values and filled circles illustrate peak-event values. Two storm events are recorded in the Wylye and the Blackwater, numbered 1 and 2, with storm 1 from 25-29 April and storm 2 from 29-30 April 2012.



a)
HAMPSHIRE AVON - Wylye Tributary
NH4-N, TP and TRP concs. (mg N/P L−1)
NO3-N conc. (mg N L−1)
TP
Nitrate
Rainfall
Flow
Flow (m3 s−1)
Rainfall (mm)
25/04
26/04
27/04
28/04
29/04
30/04
01/05
b)
WENSUM - Blackwater Tributary
TP
TRP
Nitrate
Rainfall
Flow
c)
EDEN - Newby Beck Tributary
TP
TRP
Rainfall
Flow

30

Figure 4. Plots showing nutrient response to rainfall and flow events in: (a) the Hampshire Avon Wylye tributary; (b) Wensum Blackwater tributary; and (c) Eden Newby Beck tributary.

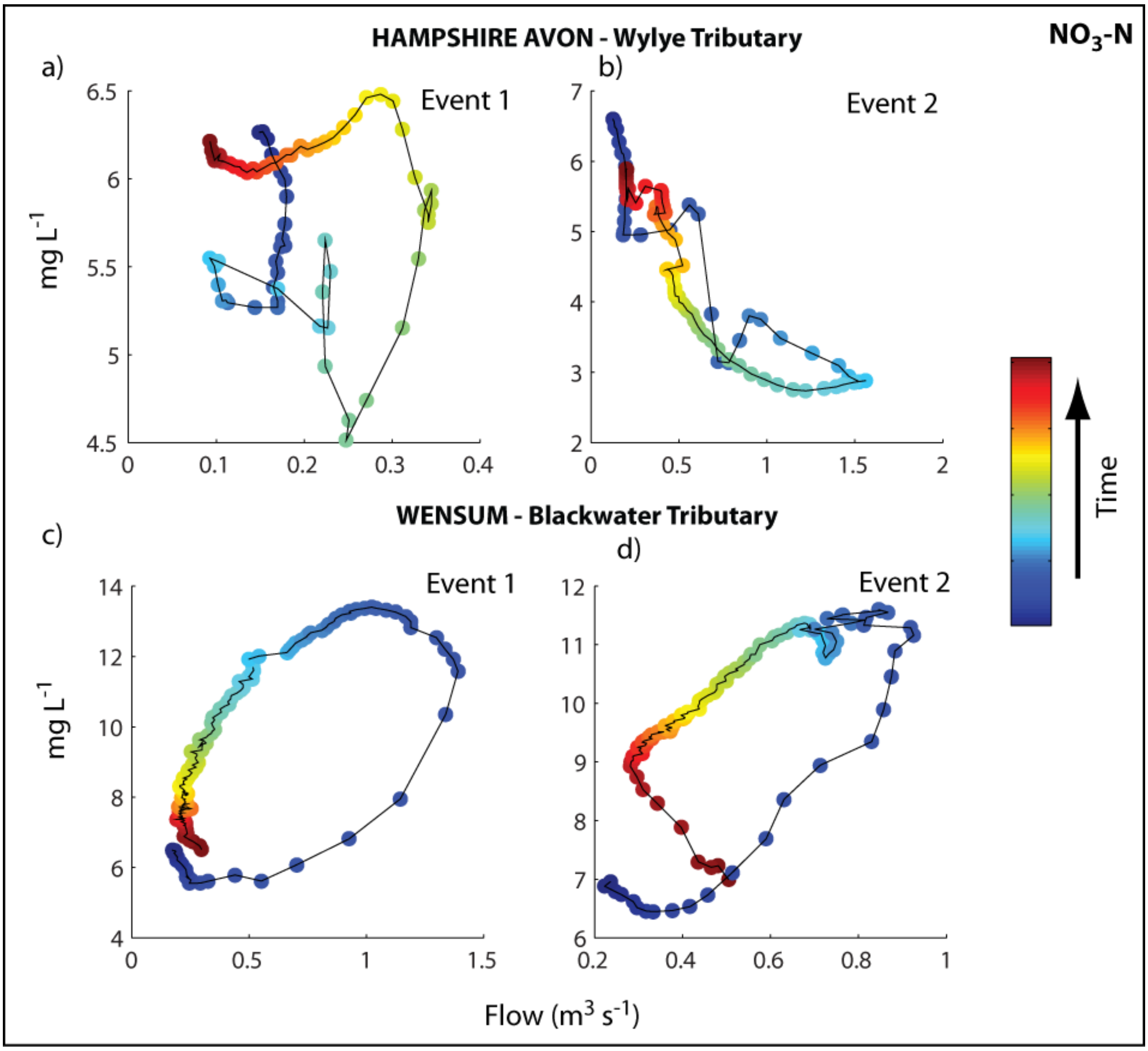


Figure 5 Plots showing hysteretic behaviour in nitrate during storm events in (a-b) the Hampshire Avon Wylye and (c-d) Wensum Blackwater tributaries.

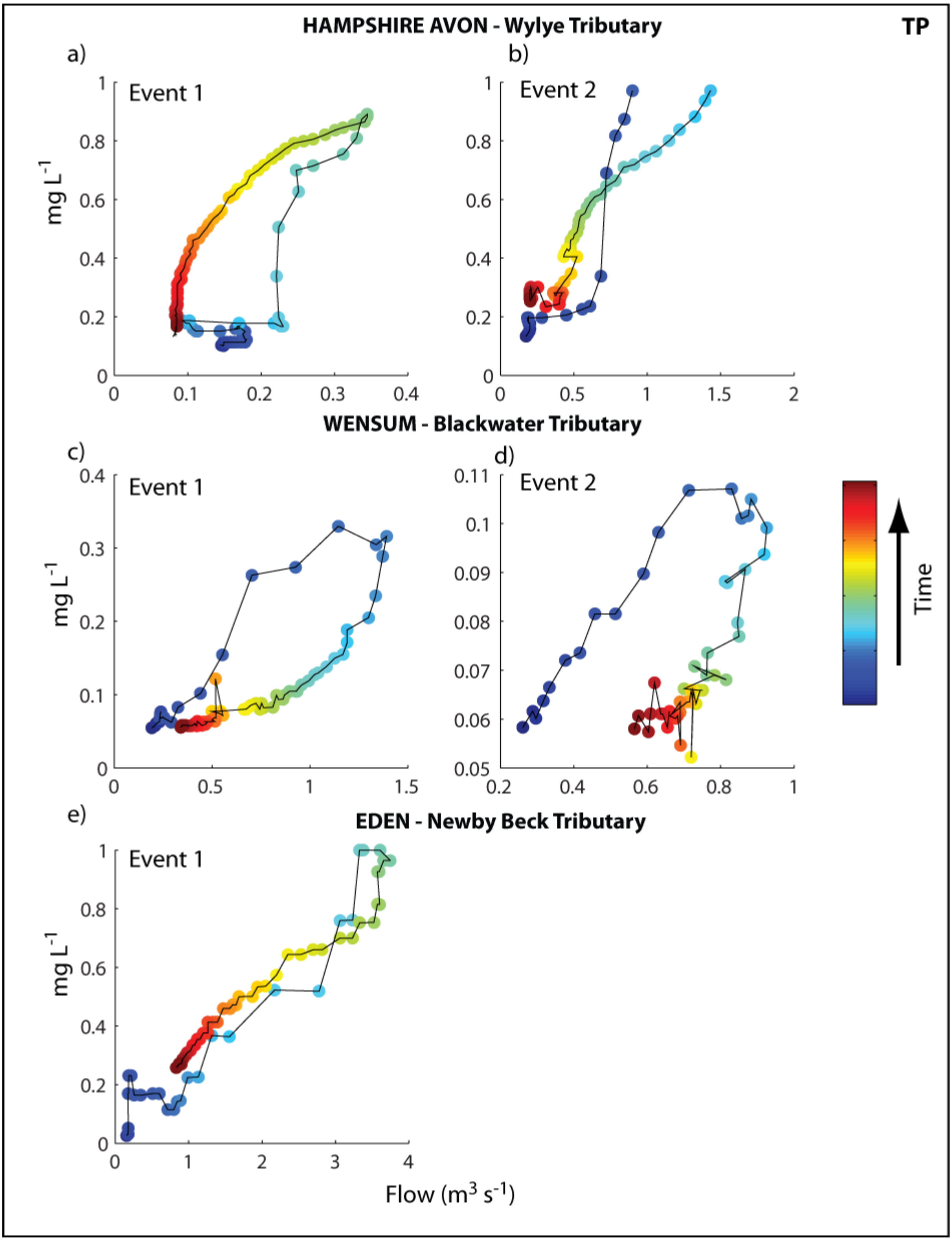


Figure 6. Plots showing hysteretic behaviour in TP during storm events in (a-b) the Hampshire Avon Wylye, (c-d) Wensum Blackwater and (e) Eden Newby Beck tributaries.

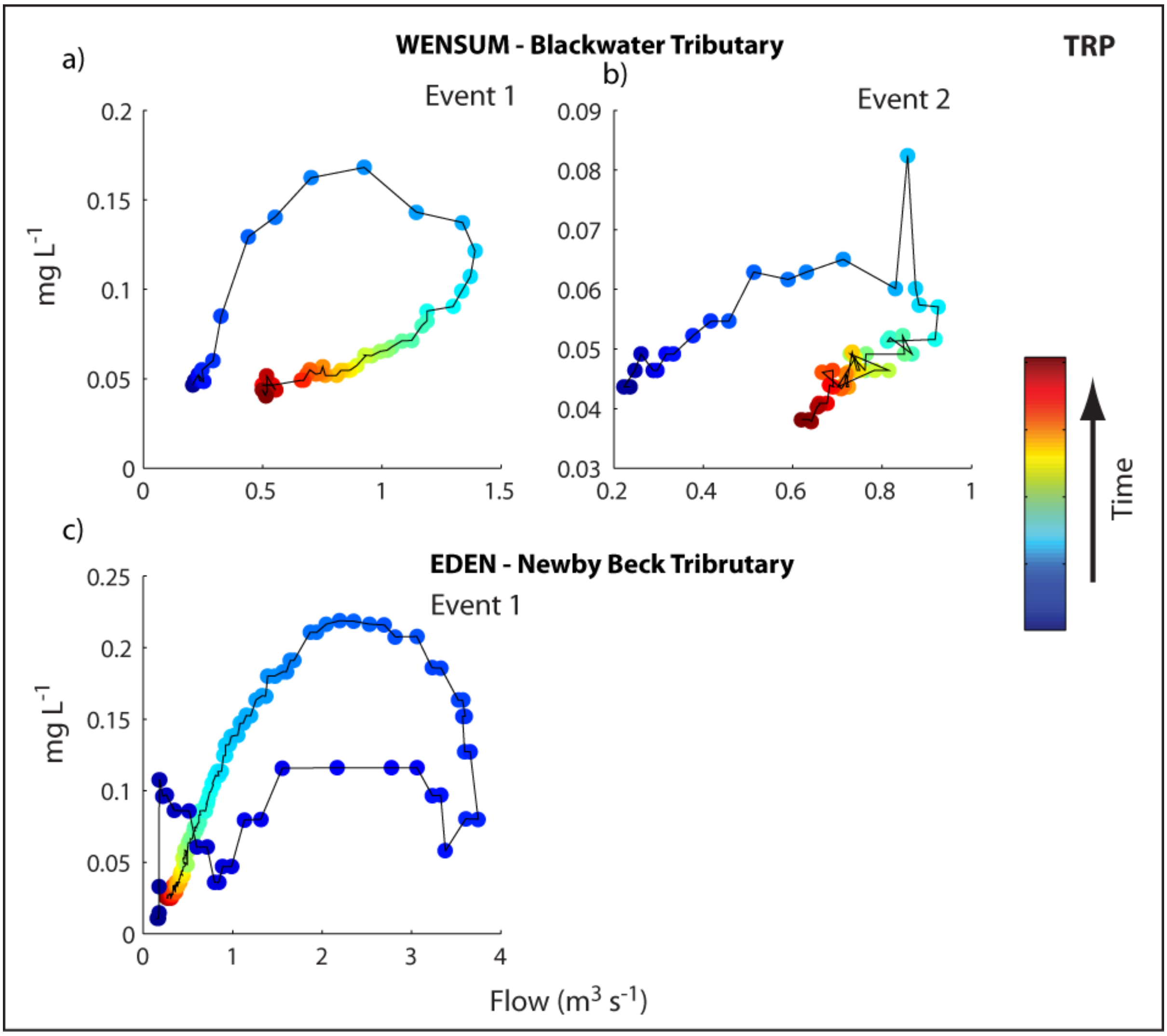


Figure 7. Plots showing hysteretic behaviour in TRP during storm events in (a-b) the Wensum Blackwater and (c) Eden Newby Beck tributaries.