High-frequency monitoring of nitrogen and phosphorus response in three rural catchments to the end of the 2011-12 drought in England

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Abstract

This paper uses high-frequency bankside measurements from three catchments selected as part of the UK Government funded Demonstration Test Catchments (DTC) project. We compare the hydrological and hydrochemical patterns during the water year 2011-12 from the Wylye tributary of the River Avon with mixed land use, the Blackwater tributary of the River

Wensum with arable land use and the Newby Beck tributary of the River Eden with grassland land use. The beginning of the hydrological year was unusually dry and all three catchments were in states of drought. A sudden change to a wet summer occurred in April 2012 when a heavy rainfall event affected all three catchments. The year-long time-series and the individual storm responses captured by *in situ* nutrient measurements of nitrate and phosphorus (total phosphorus and total reactive phosphorus) concentrations at each site reveal different pollutant sources and pathways operating in each catchment. Large storm-induced nutrient transfers of nitrogen and phosphorus to each stream were recorded at all three sites during the late April rainfall event. Hysteresis loops suggested transport-limited delivery of nitrate in the Blackwater and of total phosphorus in the Wylye and Newby Beck, which was thought to be exacerbated by the dry antecedent conditions prior to the storm. The high rate of nutrient transport in each system highlights the scale of the challenges faced by environmental managers when designing mitigation measures to reduce the flux of nutrients to rivers from diffuse agricultural sources. It also highlights the scale of the challenge in adapting to future extreme weather events under a changing climate.

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). The aim of the WFD is 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 and groundwater bodies. Enrichment of N and P is leading to 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 et al., 2011; Grizzetti et al., 2011; Leip et al., 2011). Improved nutrient removal at wastewater treatment plants has been effective at reducing point source inputs to waterbodies, which means 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; Lloyd et al., 2014) 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 water quality. Weekly sampling typically misses critical storm events, which undermines characterisation of the close coupling between hydrological and chemical dynamics, and results 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; Lloyd et al., 2014). 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). An accurate understanding of the relative contributions and timing of N and P inputs to rivers and streams is important for targeting effective mitigation (Jarvie et al., 2010). High 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; Heathwaite et al., 2006; Rozemeijer and Broers, 2007; Haygarth et al., 2012). Hysteresis patterns in concentration-discharge plots during periods of high flow can be used to compare nutrient concentrations on the rising and falling limbs of a hydrograph. Hysteresis loops 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 arise from the rapid delivery of the pollutant from source to sampling point, which suggests close proximity of the source (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 coarse suspended sediment, eroded soil and subsequent sediment delivery from upper slopes or bank seepage for pollutants more associated with particle-bound transport

(Bowes et al., 2005). Inferences of runoff pathways based on concentration-discharge plots are strongest when additional information is available about prominent hydrograph components and when source end member concentrations are available (Chanat et al., 2002). However, hysteresis plots are simple to construct and the different shapes produced can be used to infer major processes determining pollutant transport, which can inform more intensive studies of source end members and pathways using isotopes and other geochemical tracers.

The Demonstration Test Catchments (DTCs) programme in England is based in three representative catchments (Figure 1) with different landscape characteristics and farming systems. The aim of the programme is to assess whether new farming practices, targeted to reduce diffuse pollution from agriculture, can also deliver sustainable food production and environmental benefits (LWEC, 2013). Target sub-catchments have been equipped with high sampling frequency bankside stations which monitor nitrate, total phosphorus (TP) and total reactive phosphorus (TRP) concentrations in the water column at each site. Researchers are using the high-frequency data during the first phase of research to study nutrient dynamics under ‘business as usual’ farm activities before 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 hydrochemical patterns recorded in the different DTCs during the hydrological year 2011-12, including an examination a sharp transition from drought stress to flood risk across much of England in late April 2012 when a large storm moved over the country. The three study tributaries from each DTC are: the Wylye tributary in the Hampshire Avon catchment; the Blackwater Drain tributary in the Wensum catchment; and the Newby Beck tributary in the Eden catchment. Antecedent conditions, hydrochemical signals, hysteresis loops and export rates have been used to examine the possible nutrient transport mechanisms triggered in response to the unusual meteorological conditions captured in each tributary using data gathered by *in situ* monitors.

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 high base flow indices (>0.7) (Marsh and Hannaford, 2008). The Upper Greensand unit also supports the baseflow (Soley et al., 2012). The River Wylye sub-catchment is underlain by Chalk, with Upper Greensand in the west of the sub-catchment. The Upper Greensand aquifer is underlain by Gault Clay providing an impermeable layer which means that the overlying shallow aquifers can be very productive (Allen et al., 2014). Farming systems in this sub-catchment tend to be intensive mixed arable and livestock production; N fertiliser application rates on crops such as winter wheat are typically in excess of 200 kg N ha^{-1}. Diffuse sources of N and P dominate stream loads in the headwaters of the Wylye (Yates and Johnes, 2013), compromising its ecological status under the WFD.

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. A complex sequence of Quaternary strata over much of the catchment is formed of glacial tills, sands, gravels, alluvium, peat and river terrace deposits. Low permeability tills in excess of 15 m in interfluve areas restrict 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 N fertiliser application rates of around 220 kg N ha^{-1} on cereal crops. The ecological status of the Blackwater tributary is compromised by high rural N, P and sediment inputs.

The Eden Valley in Cumbria is generally underlain by Permo-Triassic sandstone, which is classed as a Principal Aquifer. Sandstone outcrop covers approximately 20% of the catchment. Superficial deposits cover the remaining 80% of sandstone and consist of glacial tills and sands and river alluvium. Generally, these superficial deposits are thin with less than 2 m thickness 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). Unlike the majority of the Eden catchment, the Newby Beck sub-catchment is underlain by low permeability glacial deposits over Carboniferous limestone. Newby Beck a typical grassland sub-catchment encompassing a mixture of dairy and beef production. Fertiliser application rates on grassland are about 56 kg N ha^{-1} and 17 kg P ha^{-1}, whereas on arable land, rates are about 127 kg N ha^{-1} with variable slurry applications for P and K. The wetter and colder 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, resulting in high inputs of sediment and associated P to receiving waters.

2.2 DTC monitoring infrastructure

Each DTC has installed a monitoring network in target sub-catchments to measure meteorological, hydrological and hydrochemical parameters. Rainfall 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 15 minute resolution at an EA flow monitoring station at Brixton Deverill. Pressure transducers housed in stilling wells in the Blackwater and Newby Beck record stage at 30-minute temporal resolution. Stage data 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. Nutrient concentration data are collected at 30-minute temporal resolution using walk-in sampling stations located in each sub-catchment. Each station is equipped with Hach Lange nutrient analysers. A Nitratax Plus SC probe is housed in a flow-through cell, which measures nitrate (as NO_3-N) using 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 and Quality Control procedures

Quality Assurance (QA) procedures are followed during data collection. The Nitratax Plus SC 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. This frequency of calibration and maintenance is sufficient to minimise drift in the *in situ* measurements.

Regular maintenance activities are carried out at different frequencies across the three sub-catchments but involve at least monthly cleaning of flow-through cells, weekly 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 extreme 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 control (QC) procedures.

QC procedures include the validation of high-frequency nutrient data using routine daily spot samples in the Wylye, weekly spot samples in the Blackwater and monthly spot samples in Newby Beck. These samples are analysed in laboratories following standard methods. Inter-laboratory comparisons are used to check consistency in analytical procedures between sub-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 1 in the supplementary material) where a positive residual represents an over estimation of nutrient concentration by the *in situ* equipment. Corrections of high-frequency data against laboratory measurements were not necessary for the data included in this manuscript.

QC procedures also include the identification of errors in all data sets. Errors flagged as critical include: periods of maintenance when the data may be unrepresentative; equipment and power failures; or data below limits of detection. Flagged data were not included in this analysis. Discharge data from the Blackwater presented here have been smoothed using a moving average window of five measurements. QA and QC procedures were followed for all data reported in this paper.

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:

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

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 concentration-discharge relationships of nitrate, TP and TRP, were investigated in each of the events in the Wylye, Blackwater and Newby Beck (Figures 5-7). To aid comparisons between events and sub-catchments, a 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 higher the index value, the greater the difference in concentration of the nutrient on the rising and falling limbs of the hydrograph (Table 4).

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 to September 2012 for nitrate, TP, discharge, rainfall and API for the Blackwater and Newby Beck and the same range of variables for the Wylye from March to September 2012. There were step changes in the Wylye discharge data which were 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, (Figure 2a). Discharge in the Wylye had relatively few individual discharge peaks relating to specific periods of rainfall, but long recessions after extended periods of rainfall when API values were high. The start of the hydrological year was very dry, with discharge increasing only at the end of April 2012. Two periods of maximum discharge occurred in May, and then again in July to August. The baseflow contribution of nitrate was around 7 mg N L^{-1} throughout the monitored period. The nearest borehole to the sampling point had an average nitrate concentration of 6.9 mg N L^{-1}. The baseflow nitrate signal was consistently diluted during storm periods. The TP record shows that some large peaks occurred in the year, reaching 1 mg P L^{-1} during the late April storm. 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 some heavier rainfall in January and March. Despite the rainfall in January 2012, discharge only responded with the onset of rainfall in March and then again in April and May for a more sustained period. The hydrograph showed long recession limbs during individual events, but to a lesser extent than the Wylye. Nitrate concentrations in the Blackwater showed dilution patterns from October to December in response to rainfall in the sub-catchment. From January onwards peaks in nitrate concentration beyond the baseflow concentrations were observed with concentration maximum of 14 mg N L^{-1}. Nitrate peaks became less pronounced by August 2012. There were large gaps in the TP record due to equipment failures. From the available record it is clear that TP concentrations responded quite rapidly to rainfall and increased discharge throughout the year and even to small events. Peak TP concentrations were commonly around 0.15 mg P L^{-1}which were much lower in the Blackwater than in the Wylye and Newby Beck sub-catchments.

In contrast to the Wylye and the Blackwater, the winter rainfall at the end of 2011 in the Newby Beck sub-catchment was fairly typical but, similar to the Wylye, Newby Beck had unusually dry conditions for the early part of 2012 until the late April event. The discharge record showed steep rising and falling limbs during individual storm events. The nitrate concentrations were much lower in Newby Beck than in the Wylye and Blackwater. However, similar to the Blackwater, the nitrate signal was diluted during periods of rainfall at the end of 2011 in Newby Beck but from April until July 2012 there were peaks in the nitrate signal in response to peak runoff. Peak nitrate concentrations were much lower than in the Blackwater, at around 6 mg N L^{-1}. Peaks in the TP signal in Newby Beck occurred very rapidly during times of rainfall with concentrations frequently exceeding 0.6 mg P L^{-1}.

3.2 Antecedent conditions and April storm response

In April 2012 there was higher than average rainfall in each DTC prior to a large storm which moved across the country between 25 and 29 April. The impact of this storm event was monitored in all three of the DTCs and marked the transition from an extreme dry period to a wet spring and summer. Table 2 summarises the rainfall characteristics in each DTC during this transition period. Both the Wylye and Blackwater had two stormflow peaks in response to this storm whereas Newby Beck had only one peak, 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 had already begun to wet up in the

Wylye and the Blackwater sub-catchments, while conditions in the Newby Beck sub-catchment were extremely dry until the storm event. API values increased to a maximum of 74, 44 and 20 in the Wylye, Blackwater and Newby Beck, respectively, during the April storm. 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 Newby Beck explained the smallest of the maximum event API values of the three sub-catchments.

To put these storms at the end of April 2012 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 sub-catchment prior to the hydrological response and at peak response during the late April event. It should be noted that there are substantial gaps in the TP and nitrate record for the Wylye and the TP record in 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), paralleling 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). In the Blackwater, by contrast, there were already 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 sub-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 a high discharge maximum was recorded (0.6% exceedance). The rainfall associated with this storm event analysis resulted in extreme flows in all three sub-catchments, regardless of antecedent soil moisture conditions.

The nitrate exceedence curve for the Wylye (Figure 3b) shows that there was little variation in concentration for the period monitored in the year. Stream nitrate concentration was 6.3 mg N L^{-1} before the rainfall commenced, which was diluted during both hydrograph events (5.3 and 2.7 mg N L^{-1} and 97.6 and 99.6% exceedance, respectively). During the second event, one of the lowest concentrations of the year was detected. 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 were amongst some of the highest nitrate concentrations recorded 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.

Pre-event TP concentrations were low in all three sub-catchments, 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 tributaries had 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 Newby Beck. During the second event in the Wylye, similarly high concentration and exceedance were recorded (0.97 mg L^{-1} and 0.02%, respectively), whereas in the Blackwater the second event a lower concentration and exceedance were recorded (0.1 mg L^{-1} and 19.4%, respectively) during the second event.

3.3 Hydrograph response

A total of 88 mm of rainfall was recorded in the Wylye during the large, drought-ending event which occurred on 25-26 April (45 mm) and 29 April (43 mm). The total rainfall in the Wylye was the highest of the three tributaries. The first amount of rainfall resulted in a small discharge maximum of 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^{3}s^{-1} on 29 April (0.1 mm h^{-1}, 361% of pre-event discharge (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. A maximum discharge of 1.4 m^{3}s^{-1} was recorded (0.3 mm h^{-1}, 699% of pre-event discharge; Figure 4b). Another 20 mm of rain was recorded between 27 and 29 April, resulting in a second discharge peak on the 29 April with a maximum flow of 0.9 m^{3}s^{-1} (0.2 mm h^{-1}, 213% of pre-event discharge). In Newby Beck the total rainfall between 25 – 27 April was 32 mm, with 79% falling on 26 April, resulting in maximum flow of 3.7 m^{3}s^{-1} (1 mm h^{-1}, 2425 % of pre-event discharge; Figure 4c). A small amount of rainfall was also recorded on 29 April, but there was little response recorded in river discharge.

3.4 Nitrate, TP and TRP chemograph response

The chemographs for nitrate, TP and TRP during the study event have showed very different responses in the Wylye, Blackwater and Newby Beck sub-catchments (Figure 4). In the Wylye, the stream nitrate chemograph 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, which peaked after maximum discharge. The nitrate chemograph had a very long recession limb which spanned several days. The peak nitrate concentration was higher in the first event. The chemograph for TP in the Wylye had a very steep rising limb and a much shallower falling limb, which peaked at the same time as discharge in the first event but slightly after in the second events. Peak TP concentrations were similar between the first and second events. TP and TRP chemographs in the Blackwater had steep rising limbs which peaked before maximum flow in the first event but had little response in the second. In Newby Beck the TP chemograph had a double peak on the steep rising limb, which peaked roughly at the same time as discharge and had a shallower falling limb. The TRP chemograph by contrast, had three small peaks, the largest of which occurred after maximum discharge, again, with a long recession limb.

Stream N and P loadings were also calculated for each rainfall event listed in Table 3, along with total stream flow volumes. 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, exporting over a tonne of N 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 slightly higher in the Wylye and Newby Beck compared to the Blackwater. The highest TP export observed was from the second event in the Wylye with an export yield of 0.01 kg P ha^{-1}. TRP exports were, again, comparable, with very similar export rates in the Blackwater and Newby Beck of around 0.004 kg P ha^{-1}.

3.5 Hysteresis response

During the first rainfall event, nitrate hysteresis plots showed anticlockwise trajectories in both the Wylye and Blackwater, but the shapes of the loops were very different. The overall trajectory of the first hysteresis loop in the Wylye was anticlockwise with a negative HI_{mid} value (Table 4), although it started in a clockwise direction (Figure 5a). The second event (Figure 5b) produced a figure-of-eight shaped loop in the Wylye which remained clockwise on the falling limb, hence the positive HI_{mid} value. In the Blackwater, the clockwise nitrate loops for both events started and ended from the bottom left of the plot (Figure 5 c and d), as opposed to the top left of the plot in the case of the Wylye. The HI_{mid} value in the Blackwater was higher for the first event than the second (Table 4).

The TP loop for the first event in the Wylye was anticlockwise (Figure 6a) with a negative HI_{mid} value (Table 4). In the second event, the loop was a figure-of-eight shape (Figure 6b), which was mostly clockwise with a positive HI_{mid} value (Table 4). The TP concentration exceeded the 1 mg P L^{-1} limit fixed by the instrument at that time. In the Blackwater, both TP (Figure 6c and d) and TRP concentrations (Figure 7c and d) produced clockwise loops in both events. Concentrations were lower in the second event, producing a substantially lower HI_{mid} value (Table 4). In Newby Beck, TP and TRP produced very different shaped loops. The TP loop was narrow but steep (Figure 6e) with a small clockwise trajectory at the beginning, followed by a second, larger clockwise trajectory for the remainder of the rising limb, which switched to an anticlockwise trajectory on the falling limb. The small HI_{mid} value was negative (Table 4). The TRP loop had two clockwise trajectories followed by a large anticlockwise trajectory on the falling limb, hence the negative HI_{mid} value (Figure 7c; Table 4).

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 (Jordan et al., 2005; Jordan et al., 2007; Halliday et al., 2014). The discharge, nitrate and TP records from the monitoring stations from a water year reveal that hydrological processes and nutrient dynamics were different between the three sub-catchments. In the Wylye, the high nitrate concentration in the chalk aquifer is likely to account for the relatively stable trend in nitrate concentrations in the channel, diluted at times of rainfall. The dilution of nitrate concentration during events is likely due to the delivery of relatively low nitrate water flushed to the stream from near-surface sources, which dilutes the relatively high nitrate water delivered to the stream from the chalk aquifer. Nitrate concentrations increased on the falling limb of the hydrograph in line with classic nitrate dilution trends reported for permeable catchments in a range of prior publications (Burt et al., 1988; Johnes and Burt, 1993). During storm events in April and July TP concentrations increased and peaked at the same time as the highest API values, representing the flushing of

P-rich near-surface sources activated during periods of high saturation in an otherwise subsurface-driven sub-catchment. This is supported by 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 with P flushing to the river from bankside septic tanks during extreme high flow events.

In the Blackwater tributary, groundwater in the underlying chalk aquifer has very low nitrate concentrations (<0.1 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 monitoring point is most likely derived from the high nitrate input of the western tributaries in the sub-catchment which have more impermeable clay soils, high nitrogen inputs from arable land and a dense network of tile drains. Weekly sampling of tile drain discharge has shown that nitrate concentrations were frequently between 3 and 20 mg N L^{-1}, with concentrations in some of the deeper more continuously flowing drains 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 is thought 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, nitrate peaks which exceeded the baseflow concentration during the recession periods of individual storms coincided with higher API values. The nitrate peaks were attributed to greater levels of saturation in the sub-catchment which would cause a greater number of tile drains to flow into tributary streams containing high nitrate concentrations from mineral fertiliser input in the upper part of the sub-catchment. The frequent occurrences of TP peaks even with small rainfall events show that P is easily mobilised. Sediment fingerprinting investigations 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 operation of rapid runoff response pathways (surface runoff and preferential flow in drains) and the lower baseflow index (Table 1) explain the flashy nature of Newby Beck. Groundwater contribution to streamflow is likely to be much less important during stormflow than in the other sub-catchments due to the depth of the aquifer, particularly after a period of drought during which groundwater recharge might be expected. The very low nitrate concentrations under baseflow conditions were due to the lower inputs from nitrogen fertilisers, as arable farming only makes up a small proportion of the land use, and there is no nitrate-rich baseflow contribution in this tributary. The series of nitrate peaks observed between April and July 2012 (Figure 2) are likely to reflect a combination of both incidental and preferential transfers of nitrate as a response to spreading of animal wastes and fertilisers, and the flushing out of mineralised nitrate which accumulated in soil runoff pathways as a result of the winter drought period. Rapid surface runoff generation exacerbated by extensive soil compaction from livestock trampling and silage production is thought to be responsible for soil erosion, resulting in the rapid response in TP concentration to increasing flow at the sampling point. Tramlines created by farm machinery also promote high connectivity between sources and receiving waters by channelling flow downslope. 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 international literature. Subsurface N transport dominates in sub-catchments with permeable soils and geology, whereas near surface P transfer dominates in sub-catchments with poor to moderately drained soils (Burt et al., 1988; Johnes and Burt, 1993; Melland et al., 2008; Melland et al., 2012; Mellander et al., 2012). In the Blackwater sub-catchment, nitrate concentration on the recession limb of storm events frequently remained elevated for several days at times of high saturation. Such long recession periods may become important for the ecological status of receiving waters as they may persist into ecologically sensitive periods, such as late spring and early summer low flows (Mellander et al., 2012) when reduced flow, higher temperatures and greater light availability favour algal growth (Mulholland and Hill, 1997). Permeable catchments such as the Wylye and the Blackwater are common throughout the UK and much of temperate northern Europe. Therefore, in catchments dominated by subsurface flow, improving groundwater quality is essential in order to support good surface water quality (Rozemeijer and Broers, 2007; Allen et al., 2014). Mitigation strategies which target reductions in nitrate leaching include the use of cover crops over winter, limiting N application prior to periods of high drainage, reducing net N inputs to the soil system, synchronising N supply with plant demand and the use of nitrification inhibitors (Di and Cameron, 2002; Hansen et al., 2007; Hooker et al., 2008; Premrov et al., 2012). Preventing the accumulation of N in the soil profile before the leaching season starts is an important step towards reducing nitrate leaching in vulnerable areas (Di and Cameron, 2002). Over time the reduction in leaching will lead to a depletion of vadose zone and groundwater stores of nitrate, which will subsequently reduce stream N loads, although this reduction may be unachievable in chalk catchments within WFD target timescales (Jackson et al., 2008).

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

In the Wylye, the API value was elevated before the late April storm and there had already been some more gradual dilutions in the baseflow nitrate concentration due to rainfall in the earlier part of April (Figure 2a). The highest API value for the entire year occurred during the second event, which coincided with a large dilution in streamwater nitrate concentration. The thickness of the unsaturated zone and the distance to the river influences the travel time of event water in chalk catchments (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 distributed travel times, resulting in anticlockwise hysteresis loops (Figure 5a and b).

The anticlockwise loops in the Blackwater (Figure 5c and d) suggest substantial transport of nitrate to the stream as opposed to the dilution of baseflow concentrations observed in the Wylye. The event studied in detail here was not the first to occur since the end of the drier than average winter period (Figure 2b) but these loops show that there was still abundant nitrate in the sub-catchment which had not been exhausted by earlier events and would, therefore, appear to be transport limited (Edwards and Withers, 2008). 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). Soil water extracted at 90 cm depth from porous pots contained 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 to winter wheat in January to April (Ferrant et al., 2013).

4.2.2 Phosphorus

In the Wylye, remobilisation of channel bed sediments deposited from the first event may account for the initial clockwise TP hysteresis in the second event (Eder et al., 2014), followed by the delayed delivery of the more distant component (Figure 6a and b), though flushing of P-rich effluent from bankside septic tanks could also account for this behaviour (Yates and Johnes, 2013). TP concentrations in both events reached a concentration of at least 1 mg P L^{-1} showing that TP sources were not exhausted by the first event which had a smaller flow volume suggesting delivery of P from diffuse catchment sources was transport limited (Edwards and Withers, 2008). 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 (Figure 2a). The lack of TP transport in March and April may indicate a build-up of P soil reserves. Other authors cite soil erosion on upper slopes, bank seepage and remobilisation of coarse bed sediment and associated P for anticlockwise hysteresis in headwater streams (Bowes et al., 2005).

In the Blackwater, clockwise TP and TRP hysteresis loops (Figure 6c and d and Figure 7a and b) indicate the flushing of a rapidly available source such as 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; Bowes et al., 2005; Cooper et al., 2013) while road runoff was also likely to be a source (Collins et al., 2010). There were several TP (Figure 2b) and TRP peaks as a result of events in March and early April. Mobilisation of P during these events may explain the rapid response in the event studied here as re-suspension of previously transported P, and would also explain source-limitation during the second event (Bowes et al., 2005; Jordan et al., 2005; Jordan et al., 2007). 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 of a storm (Djodjic et al., 2000).

The difference in shape of the TP and TRP hysteresis loops in Newby Beck indicate different sources or pathways of P in this sub-catchment (Figures 6a and 7a) (Haygarth et al., 2004). The initial clockwise trajectories for both TP and TRP maybe a result of rapid mobilisation of a source close to the steam or in the stream itself that was equally composed of reactive and particulate forms of P, perhaps due to runoff from farmyards (Hively et al., 2005; Withers et al., 2009). The second, larger TP clockwise trajectory was most likely the result of overland flow transporting particulate and colloidal P fractions, responding to the physical energy of the period of heaviest rainfall (Haygarth and Jarvis, 1997), perhaps due to soil compaction through animal grazing and farm machinery traffic. Although TRP was present, it comprised a much smaller part of the TP signal at this stage. The large anticlockwise TRP trajectory on the falling limb may be explained by the sub-surface transport of dissolved, colloidal and molybdate-reactive particulate P which had a delay in reaching the stream. As the sub-catchment wetted up and slower sub-pathways were activated, the dissolved forms of P could become well mixed and transported in the soil matrix (Haygarth et al., 2004). 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 previous storms and associated source exhaustion, unlike in the Blackwater. The event which followed had a greater discharge and API but a smaller TP peak. This finding is in agreement with 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 (Marsh and Parry, 2012). The rainfall from April-June 2012 in England was nearly three times that of the preceding three months, which had not been experienced in over one hundred years (Marsh and Parry, 2012). 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 in English catchments with differing geologies (Foster and Walling, 1978; Burt et al., 1988; Jose, 1989). The high nitrate concentrations detected instream after the drought period were attributed to severe desiccation and subsequent wetting of soil resulting in increased rates of mineralisation of organic N and nitrification. 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 due to plant uptake (Boar et al., 1995). Others point to markedly reduced P concentrations instream in dry water years compared to wetter water years (Prior and Johnes, 2002; Evans and Johnes, 2004; Evans et al., 2004); and suggest that P accumulation in the catchment, combined with reduced efficiency of delivery pathways linking source to stream, and lack of flushing of accumulated stream sediment P stores accounts for these trends. The highest particulate P concentrations recorded in a lowland river in the south of England during a three-year period were in autumn 1997 after a prolonged drought period due to the accumulation of P-rich sediment (Jarvie et al., 2002).

Although the API values show that moisture conditions were not identical among the three sub-catchments prior to the onset of the storm event that affected the whole country on the 25 April 2012, all three sub-catchments were in states of drought. The late-April storm event marked the transition from a dry winter to a wet summer in all three sub-catchments. The states of drought which commenced during 2011 could have led to the accumulation of nitrogen and phosphorus stored in the three sub-catchments. Fertiliser applications in the spring could have further contributed to the build-up of nutrients in sub-catchment soils. The increased nutrient reserves combined with high rainfall inputs in April resulted in large peak concentration exceedence (Figure 3) and fluxes (Table 3) of nitrate in the Blackwater and TP in all three sub-catchments, but particularly Newby Beck during the late April storm. Although the three sub-catchments have different characteristics, they all showed signs of transport-limited transfers of nutrients during this large event; nitrate in the Blackwater and TP in the Wylye and Newby Beck. Jordan et al. (2007) categorise such nutrient transfers as ‘acute, storm-dependent transfers’, which were found to make up 92% of the six-month TP flux in a flashy, grassland headwater catchment in Ireland. The authors state that under the WFD it is advisable to implement catchment management necessary to reduce diffuse transfers of this type to reduce the annual P flux to receiving waterbodies. This paper supports this finding and proposes that the same principle applies to the acute storm-dependent nitrogen transfer in the Blackwater and other lowland, under-drained, arable catchments throughout temperate Europe. The total proportion of agricultural land that is underdrained in Europe can range from 33% in the UK to 93% in Finland (De la Cueva, 2006). The high nutrient transfers identified here underscore 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. Environmental factors, such as prolonged dry periods, exacerbate the challenge by increasing the likelihood of acute flushes of pollution when rainfall does occur. Future mitigation options available to land managers need to reflect the heterogeneity of pollutant sources and pathways acting across different landscapes and land use under 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 characterisation of catchments using semi-continuous hydrological and hydrochemical datasets avoids bias towards particular sampling regimes. Extreme events, such as recorded here, can be put in the context of the actual range of variation in complete hydrological years, which is often unknown without high frequency measurements. Even in cases where automatic samplers are triggered several times per year, key storm transfers may be missed outside of deployment periods and details such as the number of bottles available or the trigger threshold may dictate whether selected events are captured in full. High-frequency monitoring equally captures fine-scale patterns during baseflow which may highlight new avenues for research on catchment nutrient transfer processes, such as the significance of chronic less rainfall dependent P transfers on the eutrophic state of streams during low flows (Jordan et al., 2005).

Hysteresis is usually not taken into account in load estimation techniques (Eder et al., 2010). The hysteresis loops constructed for the three sub-catchments during the period studied here reveal differences between the study areas and among events within the same sub-catchment. 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

Hydrochemical trends in three different sub-catchments have been identified using high-frequency water quality data as part of the DTC project. Data from such long-term monitoring infrastructure can be used to investigate relationships between potential environmental influences on water quality, such as meteorological conditions, as discussed here, or land use change using on-farm interventions, to be explored in the second phase of the DTC project. Hysteresis loops are simple to construct from high-frequency chemistry and discharge data and form a good basis for informing further research into catchment processes. Hysteresis patterns also highlight the complex relationship between discharge and concentration, where high-frequency data, such as those demonstrated here, are essential for improving load estimation. In agreement with other authors we have identified acute, storm-dependent transfers of P in all three sub-catchments as a result of a large storm following a dry period. In addition, we identified acute, storm-dependent transfers of N in the drained, lowland, arable Blackwater sub-catchment. Such storm transfers are likely to be repeated in similar catchments throughout Europe and require focused mitigation in order to achieve WFD targets. The spectrum of pollution sources and pathways highlighted by the high-frequency monitoring represents the continuing challenge for environmental managers in mitigating against nutrient pollution from diffuse catchment sources, and also in responding to climate change. Emerging research initiatives in the UK and elsewhere, including the DTC programme, 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 in nutrient-enriched catchments.

Acknowledgements

The DTC programmes in the Eden, Hampshire Avon and Wensum catchments are funded by the Department for Environment, Food and Rural Affairs (Defra) (projects WQ0210, WQ0211 and WQ0212, respectively) and are further supported by the Welsh Assembly Government and the Environment Agency. The Eden project consortium (Eden DTC, www.edendtc.org.uk) includes Lancaster University, University of Durham, Newcastle University, Eden Rivers Trust, Centre for Ecology and Hydrology, British Geological Survey and Newton Rigg College. The Hampshire Avon project consortium (Avon DTC, http://www.avondtc.org.uk/) includes Rothamsted Research-North Wyke, ADAS, Queen Mary University of London, the Universities of Bristol, Exeter and Reading, and the Game and Wildlife Conservation Trust. The Wensum project consortium (Wensum DTC, www.wensumalliance.org.uk) includes the University of East Anglia, the Environment Agency, Anglian Water Services Ltd, British Geological Survey, Farm Systems & Environment, NIAB-TAG, Cranfield University and AMEC plc. All three consortia are grateful for the assistance of farmers and land owners in their relevant sub-catchments for providing access to monitoring sites.

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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]
Land use	Livestock and cereals	Arable crops	Livestock

Table 2. 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 3. Nutrient fluxes for each storm event in the Wylye, Blackwater and Newby Beck as absolute load and export.

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

Table 4. Summary of the hysteresis index values, HI_{mid}, for nitrate, TP and TRP 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

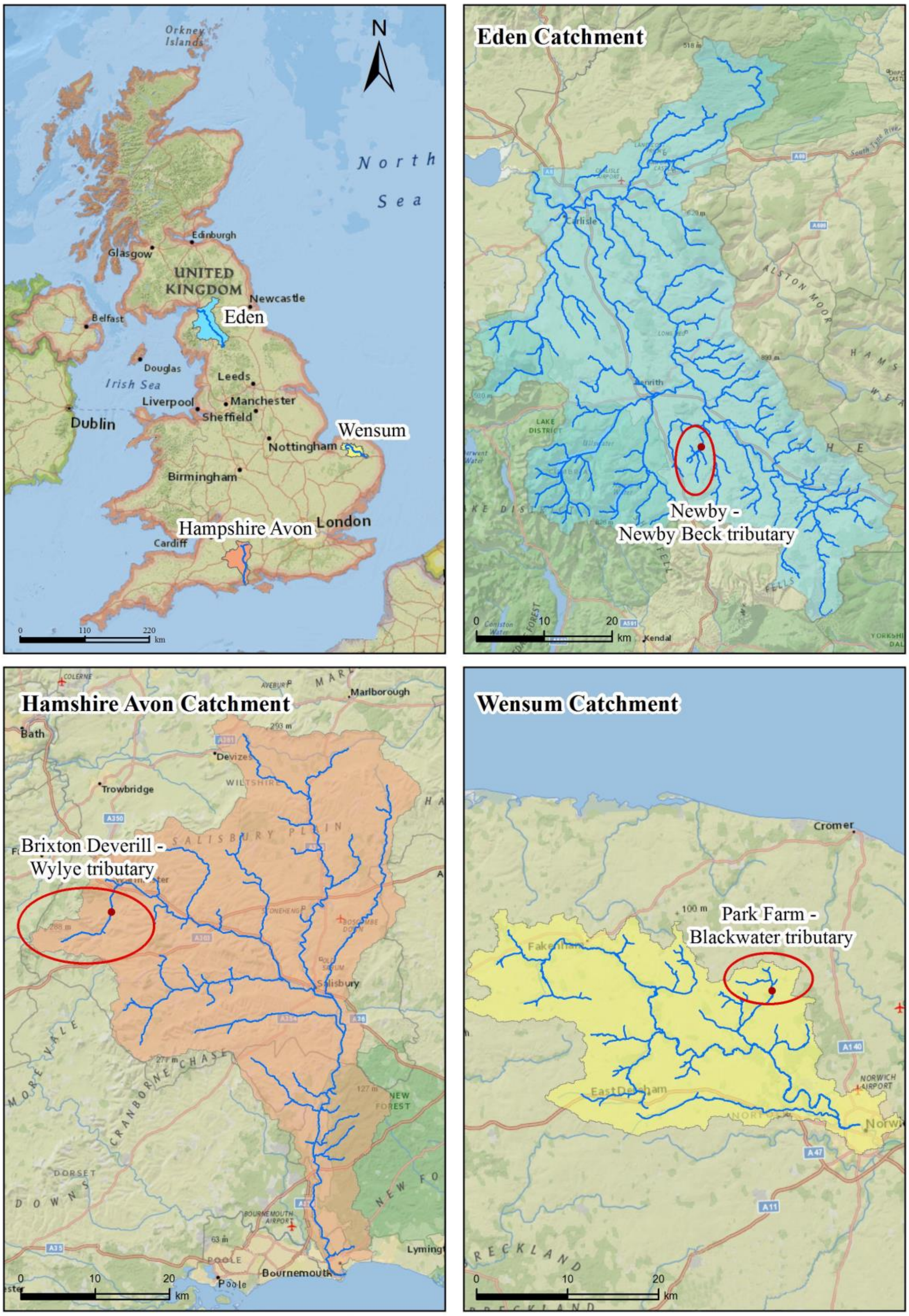

Figure 1. Location map of the UK showing the three Demonstration Test Catchments, the Hampshire Avon, Wensum and Eden; and the respective tributaries in each catchment, the

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

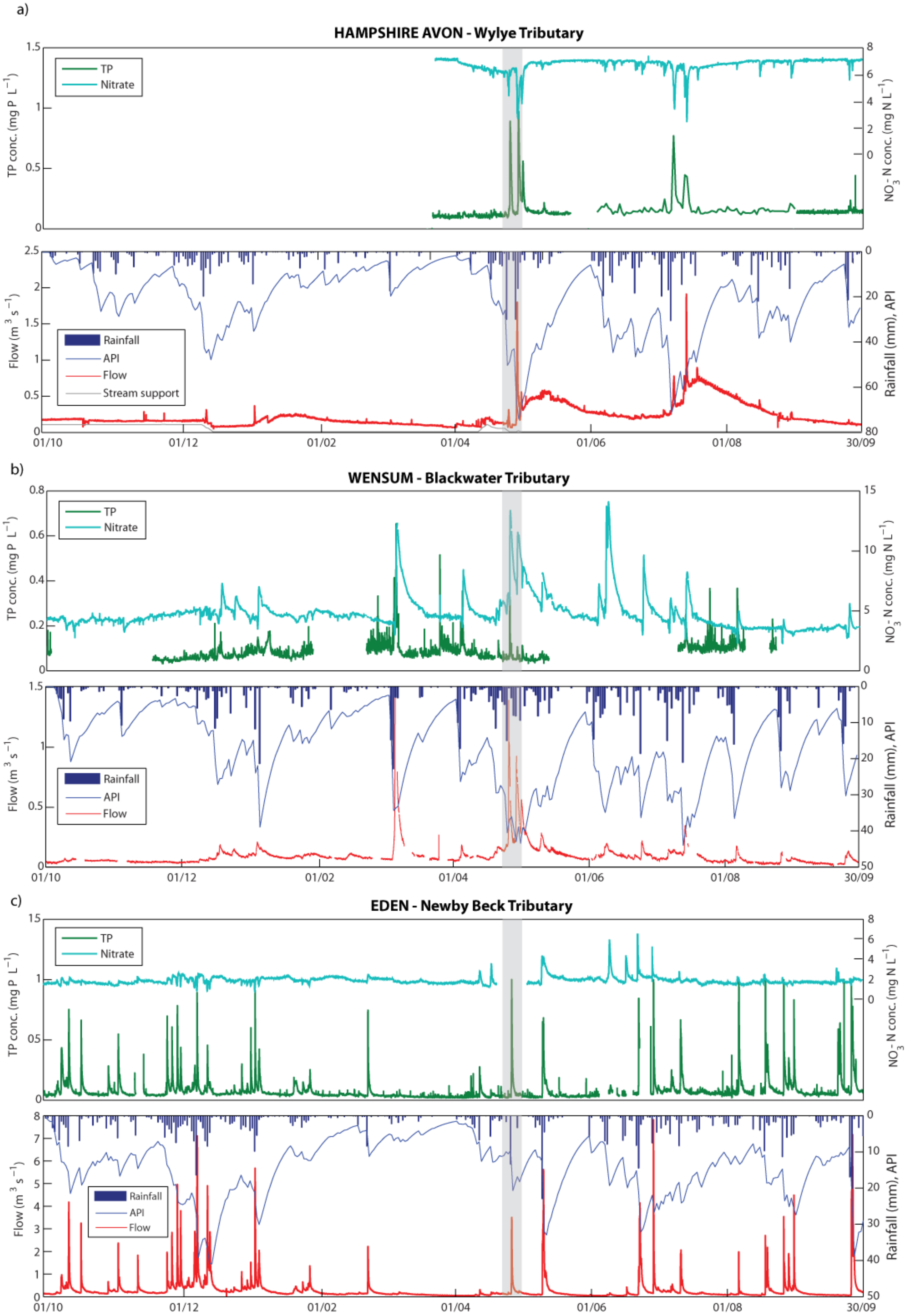
a)
HAMPSHIRE AVON - Wylye Tributary
TP conc. (mg P L^{-1})
NO$_3^-$-N conc. (mg N L^{-1})
TP
Nitrate
Flow (m^3 s^{-1})
Rainfall (mm), API
Rainfall
API
Flow
Stream support
01/10
01/12
01/02
01/04
01/06
01/08
30/09
b)
WENSUM - Blackwater Tributary
TP conc. (mg P L^{-1})
NO$_3^-$-N conc. (mg N L^{-1})
TP
Nitrate
Flow (m^3 s^{-1})
Rainfall (mm), API
Rainfall
API
Flow
01/10
01/12
01/02
01/04
01/06
01/08
30/09
c)
EDEN - Newby Beck Tributary
TP conc. (mg P L^{-1})
NO$_3^-$-N conc. (mg N L^{-1})
TP
Nitrate
Flow (m^3 s^{-1})
Rainfall (mm), API
Rainfall
API
Flow
01/10
01/12
01/02
01/04
01/06
01/08
30/09

Figure 2. Plots showing rainfall, river 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).

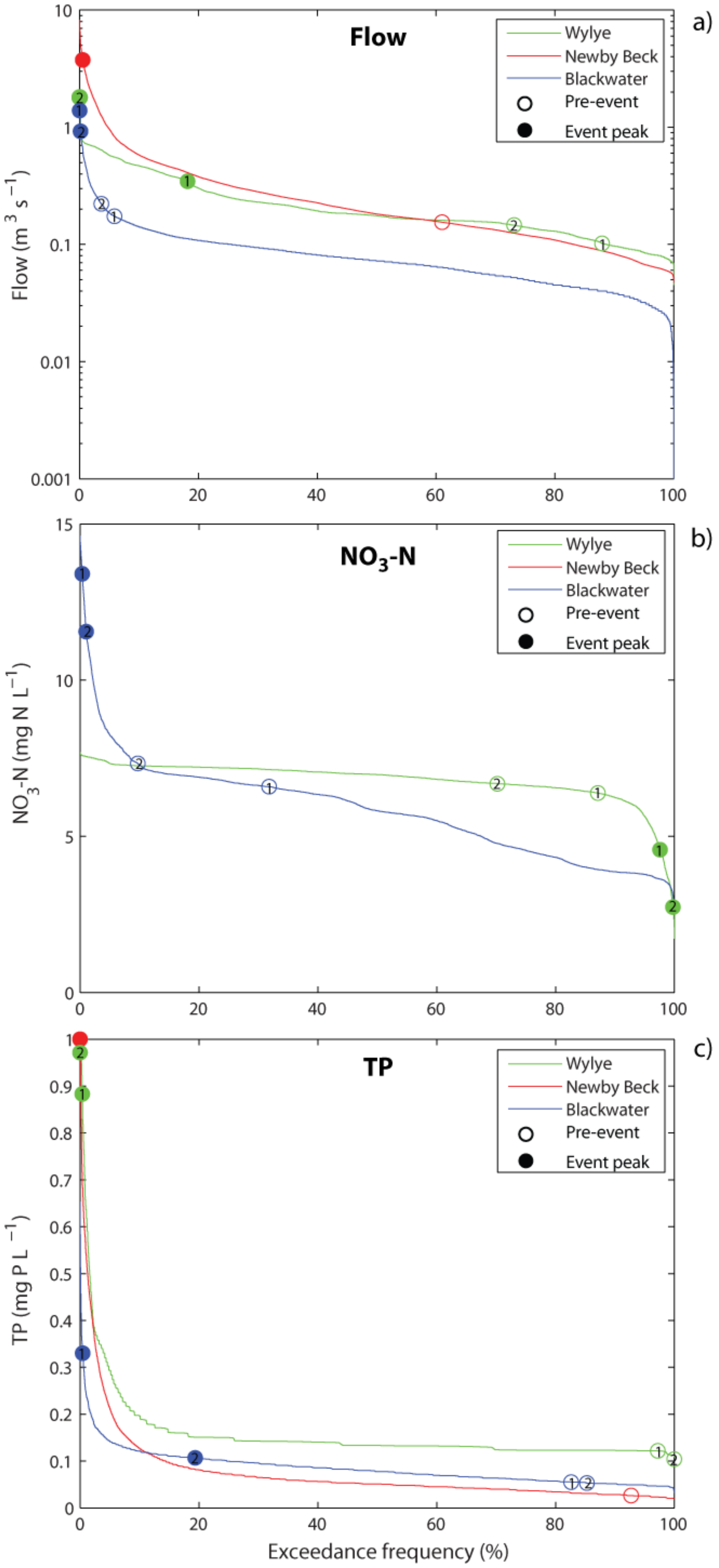
a)
Flow
Wylye
Newby Beck
Blackwater
Pre-event
Event peak
Flow (m^3 s^{-1})
10
1
0.1
0.01
0.001
0
20
40
60
80
100
1
2
b)
NO$_3$-N
Wylye
Newby Beck
Blackwater
Pre-event
Event peak
NO$_3$-N (mg N L^{-1})
15
10
5
0
0
20
40
60
80
100
c)
TP
Wylye
Newby Beck
Blackwater
Pre-event
Event peak
TP (mg P L^{-1})
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
80
100
Exceedance frequency (%)

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.

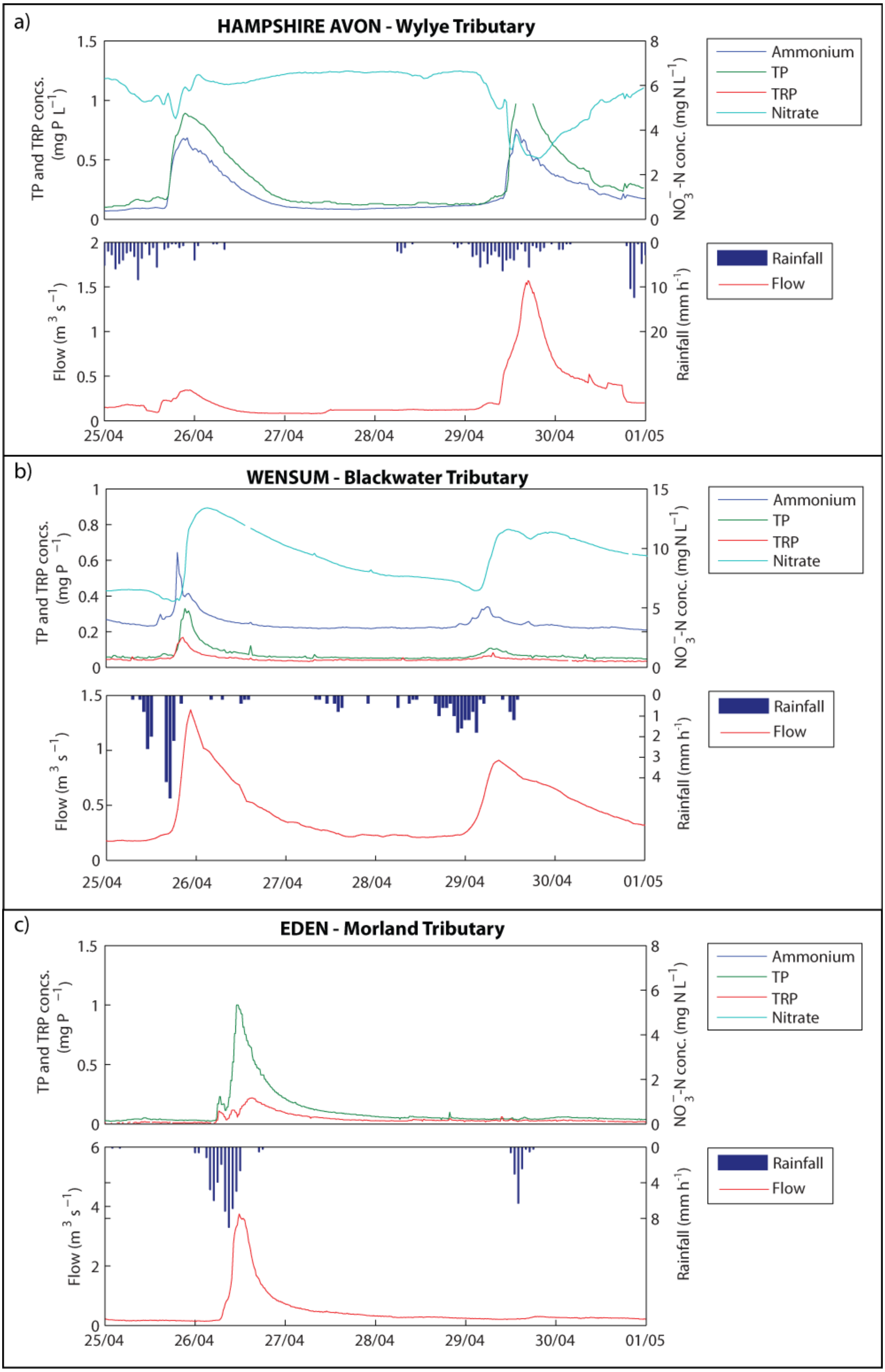
a)
HAMPSHIRE AVON - Wylye Tributary
TP and TRP concs. (mg P L^{-1})
NO$_3^-$-N conc. (mg N L^{-1})
Ammonium
TP
TRP
Nitrate
1.5
1
0.5
0
8
6
4
2
0
Flow (m^3 s^{-1})
Rainfall (mm h^{-1})
Rainfall
Flow
2
1.5
1
0.5
0
0
10
20
25/04
26/04
27/04
28/04
29/04
30/04
01/05
b)
WENSUM - Blackwater Tributary
TP and TRP concs. (mg P L^{-1})
NO$_3^-$-N conc. (mg N L^{-1})
Ammonium
TP
TRP
Nitrate
1
0.8
0.6
0.4
0.2
0
15
10
5
0
Flow (m^3 s^{-1})
Rainfall (mm h^{-1})
Rainfall
Flow
1.5
1
0.5
0
0
1
2
3
4
25/04
26/04
27/04
28/04
29/04
30/04
01/05
c)
EDEN - Morland Tributary
TP and TRP concs. (mg P L^{-1})
NO$_3^-$-N conc. (mg N L^{-1})
Ammonium
TP
TRP
Nitrate
1.5
1
0.5
0
8
6
4
2
0
Flow (m^3 s^{-1})
Rainfall (mm h^{-1})
Rainfall
Flow
6
4
2
0
0
4
8
25/04
26/04
27/04
28/04
29/04
30/04
01/05

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.

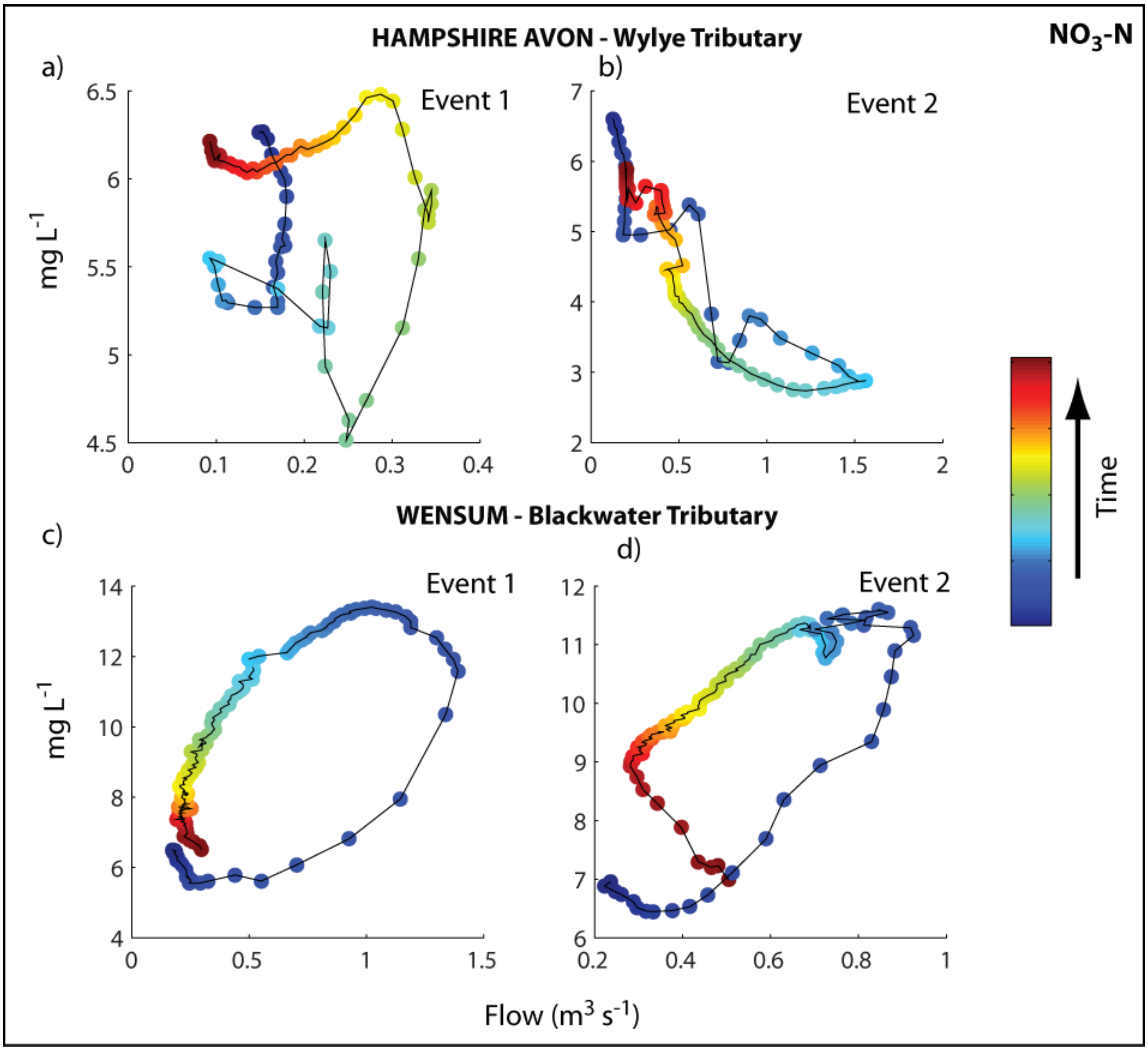

Figure 5 Concentration-discharge plots showing nitrate hysteresis during storm events in (a-b) the Hampshire Avon Wylye and (c-d) Wensum Blackwater tributaries.

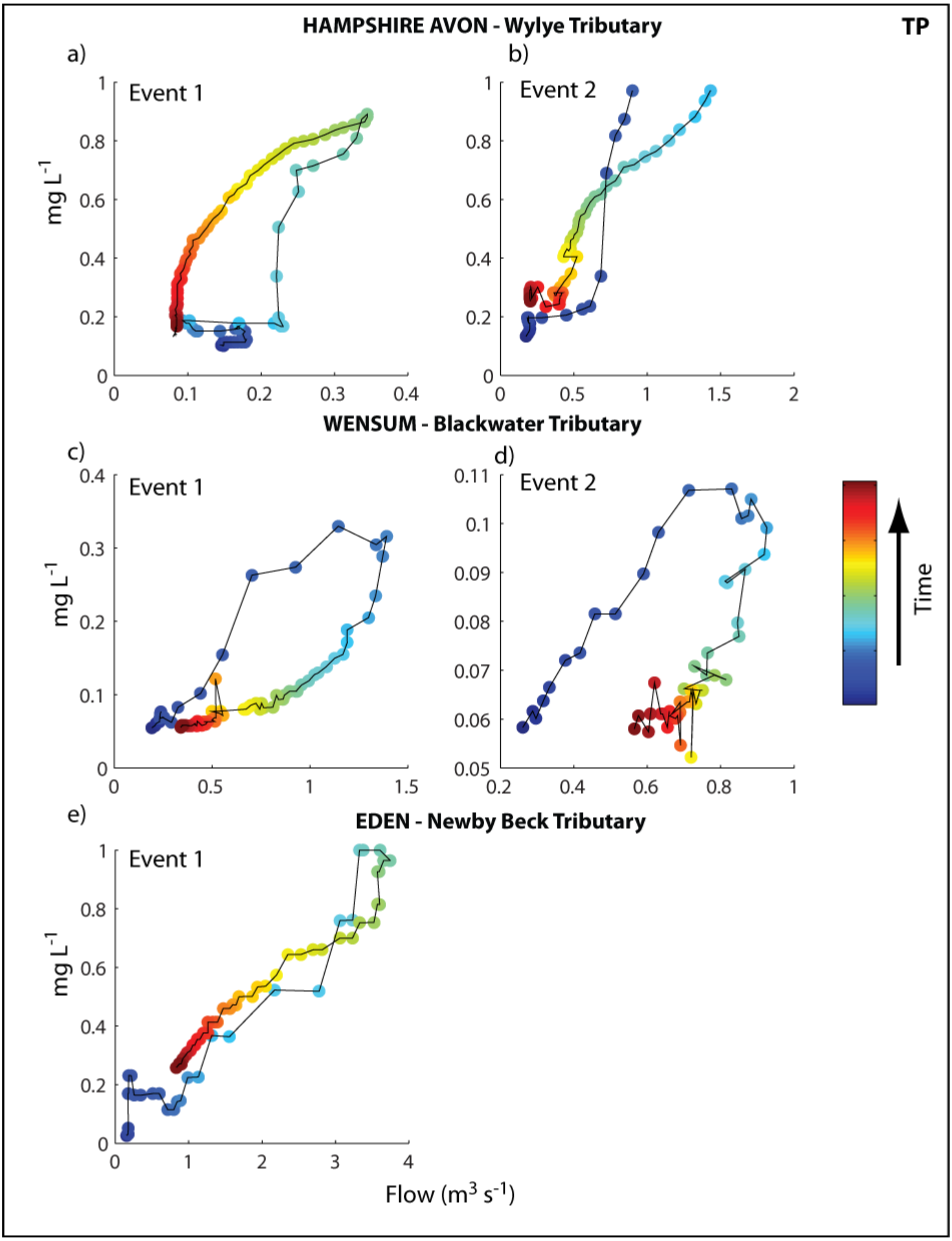

Figure 6. Concentration-discharge plots showing TP hysteresis during storm events in (a-b) the Hampshire Avon Wylye, (c-d) Wensum Blackwater and (e) Eden Newby Beck tributaries.

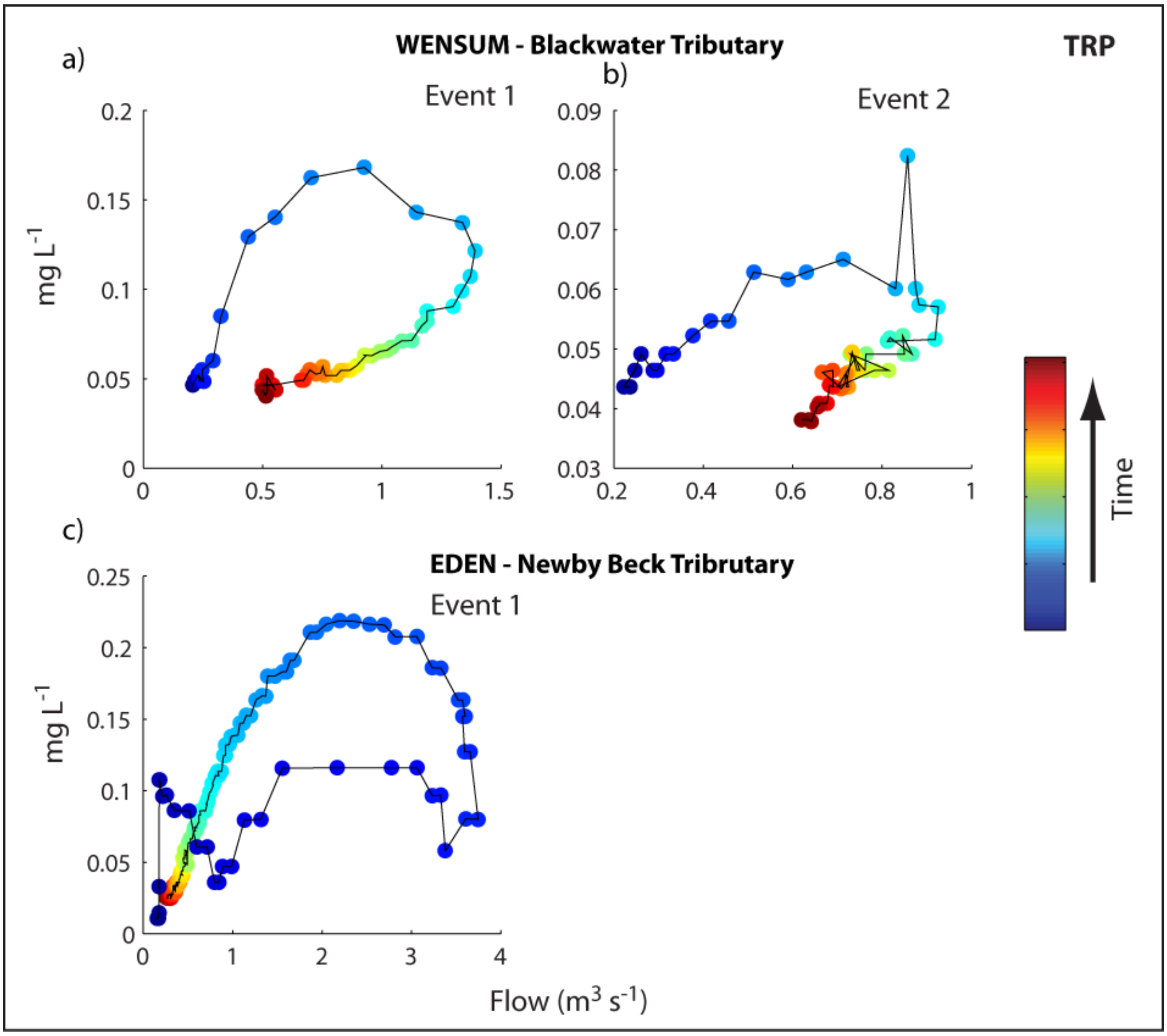

Figure 7. Concentration-discharge plots showing TRP hysteresis during storm events in (a-b) the Wensum Blackwater and (c) Eden Newby Beck tributaries.