Hydrol. Earth Syst. Sci. Discuss., 10, 15119–15165, 2013
www.hydrol-earth-syst-sci-discuss.net/10/15119/2013/
doi:10.5194/hessd-10-15119-2013

Hydrology and Earth System Sciences
Open Access
Discussions

High-resolution monitoring of catchment nutrient response to the end of the 2011–2012 drought in England, captured by the demonstration test catchments

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Received: 15 November 2013 – Accepted: 28 November 2013 – Published: 11 December 2013

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

The Demonstration Test Catchments (DTC) project is a UK Government funded initiative to test the effectiveness of on-farm mitigation measures designed to reduce agricultural pollution without compromising farm productivity. Three distinct catchments in England have been chosen to test the efficacy of mitigation measures on working farms in small tributary sub-catchments equipped with continuous water quality monitoring stations. The Hampshire Avon in the south is a mixed livestock and arable farming catchment, the River Wensum in the east is a lowland catchment with predominantly arable farming and land use in the River Eden catchment in the north-west is predominantly livestock farming. One of the many strengths of the DTC as a national research platform is that it provides the ability to investigate catchment hydrology and biogeochemical response across different landscapes and geoclimatic characteristics, with a range of differing flow behaviours, geochemistries and nutrient chemistries.

Although numerous authors present studies of individual catchment responses to storms, no studies exist of multiple catchment responses to the same rainfall event captured with in situ high-resolution nutrient monitoring at a national scale. This paper brings together findings from all three DTC research groups to compare the response of the catchments to a major storm event in April 2012. This was one of the first weather fronts to track across the country following a prolonged drought period affecting much of the UK through 2011–2012, marking an unusual meteorological transition when a rapid shift from drought to flood risk occurred. The effects of the weather front on discharge and water chemistry parameters, including nitrogen species (NO_3-N and NH_4-N) and phosphorus fractions (total P (TP) and total reactive P (TRP)), measured at a half-hourly time step are examined.

When considered in the context of one hydrological year, flow and concentration duration curves reveal that the weather fronts resulted in extreme flow, nitrate and TP concentrations in all three catchments but with distinct differences in both hydrographs and chemographs. Hysteresis loops constructed from high resolution data are used to

highlight an array of potential pollutant sources and delivery pathways. In the Hampshire Avon DTC, transport was dominated by sub-surface processes, where phosphorus, largely in the soluble form, was found to be transport-limited. In the Wensum DTC, transport was largely dominated by rapid sub-surface movement due to the presence of under-drainage, which mobilised large quantities of nitrate during the storm. In the Eden DTC, transport was found to be initially dominated by surface runoff, which switched to subsurface delivery on the falling limb of the hydrograph, with the surface delivery transporting large amounts of particulate phosphorus to the river, with a transport-limited response. The lack of exhaustion of nutrient delivery in response to such extreme flow generation indicates the size of the nutrient pools stored in these catchments, and highlights 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.

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) which 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 ground waterbodies resulting in non-compliance with legislation, albeit with different sources, 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). As point sources of pollutants become increasingly controlled, 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). In England, the Environment Agency (EA) is the "competent authority" for delivering the WFD by assessing the impact of human activity on water quality in 11 River Basin Districts (RBDs), monitoring the status of around 4500 waterbodies, preparing River Basin Management Plans (RBMPs) and selecting and targeting Programmes of Measures (POMs) recommended for each district (EA, 2013). The current water quality monitoring performed by the EA, 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 health for a number of reasons. 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 UK Government acknowledges the importance of evidence in policy making (Defra, 2005), where the use of monitoring data in decision making is not only an efficient use of resource, but will also allow more reliable and transparent decisions to be made (Collins et al., 2012). The Demonstration Test Catchments (DTCs) programme in England is a project funded by the UK government's Department for Environment Food and Rural Affairs (Defra), which has brought together researchers, practitioners

and stakeholders from multiple disciplines. Three representative catchments across England were chosen to host "research platforms" to investigate whether new farming practices, which aim to reduce diffuse pollution from agriculture, can also deliver sustainable food production and environmental benefits (LWEC, 2013). High temporal resolution monitoring equipment has been installed, including the bank-side analysis of nitrate, ammonium, total phosphorus (TP) and total reactive phosphorus (TRP) concentrations, with the aim of detecting change in water quality at the sub-catchment scale after the implementation of a variety of different mitigation measures on participating farms. The three catchments were chosen to represent different rural landscapes and farming systems typical of England. The Hampshire Avon in the south of England is a lowland river draining Chalk and Greensand landscape, with freely draining soils used for mixed agriculture; the River Wensum in the east of England is a lowland Chalk river with poorly drained soils used for arable agriculture; and the River Eden in the north-west of England drains the uplands of the Pennines with rough grazing as the dominant land use in the headwaters, draining down onto intensively farmed grazing land.

The initial stages of the project required the establishment of a consortium of partners in each DTC to shape and deliver the applied research. The monitoring infrastructure was installed from March 2011 onwards and since then "business as usual" farm operations have been monitored and the data gathered have been interpreted by each consortium with regular reporting mechanisms to farmers, consortium members and policy makers. Mitigation measures have been deployed during 2013, alongside appropriate control monitoring locations. The consortia are modelled on the experience of successful catchment management groups such as the South East Queensland Healthy Waterways Partnership in Australia (Healthy Waterways, 2013) and the Agricultural Catchments Programme in Ireland (Teagasc, 2013), that have demonstrated success in bringing together people and agencies, building trust and understanding shared problems and solutions.

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). Numerous authors present studies of individual catchment responses to storms, however, to our knowledge no studies exist of multiple catchment responses to the same rainfall event captured with in situ high resolution nutrient monitoring at a national scale. Rainfall events across the UK are often varied and localised but a large storm in April 2012 affected all three DTCs during a period of unusual weather patterns across the whole of the UK. March was exceptionally warm and the lowest rainfall since 1953 was recorded (Marsh and Parry, 2012a). Severe drought, resulting in a hosepipe ban from the first week of April, affected 20 million consumers, with soils reaching the driest state on record for the time of year (Marsh and Parry, 2012b). In stark contrast, April was the coldest since 1989 and the second wettest since records began in 1766 (Eden, 2012), with much of the existing drought region receiving more than twice its average rainfall (Marsh and Parry, 2012a). This extreme rainfall caused a dramatic hydrological transformation, which switched the focus from drought stress to flood risk in many parts of the country (Marsh and Parry, 2012b).

The aim of this paper is to examine the hydrological and chemical responses to the greatest flow events generated by the wet weather in April 2012 during the unprecedented transition from drought stress to flood risk. Rainfall, discharge, nitrate, ammonium, TP and TRP data collected from monitoring stations in each DTC catchment: at Brixton Deverill on the Wylye tributary in the Hampshire Avon; Park Farm on the Blackwater Drain tributary in the Wensum; and Morland on the Newby Beck tributary in the Eden. Antecedent conditions from the previous month, and flow and nutrient exceedance curves for the hydrological year 2011–2012 are used to put the hydrological and hydrochemical response of each catchment to storm conditions into context. Hysteresis loops and export rates have been constructed to examine the possible transport mechanisms occurring for each nutrient type at each site in response to these unusual meteorological conditions. Whilst the data presented from this storm 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 DTC catchment responses triggered by a large national storm event and, therefore, pressures acting in each DTC, thus demonstrating the value of a national research platform for understanding the responses of different catchment typologies.

2 Methodology

2.1 Site descriptions

The location of the three DTCs is shown in Fig. 1 and Table 1 provides a summary of the main characteristics of each catchment. In the Hampshire Avon, the River Wylye flows through areas of Chalk and Greensand, both of which are underlain by a clay layer with steep-sided Chalk valley slopes. Farming systems in this sub-catchment tend to be intensive mixed arable and livestock production, and the river experiences both nutrient and sediment pressures. In the Wensum, a typical lowland Chalk catchment in Norfolk, the western reach of the Blackwater tributary is underlain by glacial tills with clay-rich, seasonally wet soils on chalky boulder clay, whereas in the eastern reach the deposits comprise glacial sands and gravels with well drained sandy loam soils. The Blackwater catchment is used for intensive arable production and experiences pressures from both sediment and nutrient fluxes. In the Eden in Cumbria, the Morland 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. The harsher climate in the Eden catchment means there are fewer optimal days for cultivation so that seed beds are established in suboptimal conditions. This often results in less vegetation cover and in some cases, no establishment at all, resulting in pollution pressures from sediment and phosphorus.

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 min resolution. In the Hampshire Avon DTC, discharge is measured by an adjacent EA flow monitoring station at Brixton Deverill. The monitoring points in the Wensum and Eden DTCs are equipped with pressure transducers in stilling wells to provide a continuous 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 Wensum and Eden DTCs. Nutrient concentration data are collected at 30 min temporal resolution using walk-in sampling stations located in each DTC. The stations are equipped with Hach Lange nutrient analysers including a Nitratax Plus SC probe which measures nitrate concentrations (as NO_3-N) via an optical sensor and a Phosphax Sigma wet chemistry analyser in combination with a Sigmatax SC sampling and homogenisation unit to measure phosphorus (as TRP and TP), as documented elsewhere (Owen et al., 2012; Wade et al., 2012). In addition, ammonium concentrations (as NH_4-N) are determined every 15 or 30 min using an ion selective electrode sensor on a YSI 6600 V2 sonde.

2.3 Storm event description

The period 25–29 April 2012 was wet and stormy, as the polar front jet stream steered a number of low pressure systems across the southern half of the UK with heavy, thundery showers. During the 25 and 26 of April, a deep low and associated front tracked slowly north-eastwards across England and Wales, causing localised flooding. In order to provide a national context for the rainfall events in the monitored catchments the Weather Research and Forecasting ARW model (Skamarock and Klemp, 2008)

was used to provide national daily rainfall fields for the UK. National scale rainfall fields are generated from a 27 km two-way interactive nested configuration, with 35 vertical layers, forced and initialised using 1.0° 6 hourly analyses from the Global Forecasting System (GFS) model, with nudging towards the GFS analysis to minimise model drift. Daily sea surface temperature forcing, interpolated to a 6 hourly resolution, is provided by the Real-Time Global Sea Surface Temperature Analysis (RTG_SST), at 0.5° resolution (NCEP, 2013). Standard model setup was otherwise used, with cumulus parameterisation enabled. The model output is shown in Fig. 2 with daily rainfall totals for each of the days studied alongside sea level pressure charts (Fig. 2a–e) and a 5 day rainfall total map for the whole period (Fig. 2f). This impact of this storm event was observed in all three of the DTCs and marked the transition between a period of extremely dry weather during winter 2011 and the wet spring 2012. Table 2 summarises the rainfall characteristics in each DTC.

3 Results

3.1 Antecedent conditions

Despite the higher than average rainfall rates in each DTC for the early part of April, river discharge at the monitoring sites only responded to the onset of rainfall on the 25 April 2012 (Fig. 3). This is likely to be due to the slow recovery after soil moisture deficits reached the lowest on record for the time of year following the dry weather and exceptionally steep recessions in river flows during March. As April advanced, shallow soils became saturated and river discharges across the UK increased dramatically (Marsh and Parry, 2012b). Both the Hampshire Avon and Wensum DTCs experienced two hydrological events in response to two low pressure systems and their associated fronts, as a secondary depression formed on the back of the first, with southern England continuing to be exposed to unsettled conditions by the 29 April. Conditions were clearer in the north; hence, the Eden DTC experienced only one event, on the 25 April.

To put these storms 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 (October 2011–September 2012). These plots show the conditions in each catchment prior to the hydrological response and at peak response during the events studied here (Fig. 4). The flow duration curve plot (Fig. 4a) shows that prior to the onset of the first event in the Hampshire Avon DTC, 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 Wensum DTC, 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). The Eden DTC had a higher relative flow than the Hampshire Avon DTC 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-N duration curve (Fig. 4b) shows that for the Hampshire Avon DTC 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, particularly for the second event, when one of the lowest concentrations of the year was detected (97.6 and 99.6 % exceedance, respectively). In contrast, nitrate-N concentrations in the Wensum DTC prior to both events were relatively high (6.5 and 7.0 $\mathrm{mg\,N\,L^{-1}}$ and 31.8 and 9.7 % exceedance, respectively), reflecting the impact of the already increasing flows on nitrate mobilisation as throughflow. The peak responses produced some of the highest nitrate concentrations detected in the hydrological year (13.5 and 11.6 $\mathrm{mg\,N\,L^{-1}}$ and 0.8 and 1 % exceedance, respectively) showing a strong source of nitrate in the catchment delivered during peak flow conditions. There were no

nitrate-N data for the Eden DTC during this event as the nitrate sensor was not working during this event.

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 $\mathrm{mg\,P\,L^{-1}}$ and 97.2 %, respectively, in the Hampshire Avon; 0.03 $\mathrm{mg\,P\,L^{-1}}$ and 82.6 %, respectively, in the Wensum and 0.03 $\mathrm{mg\,P\,L^{-1}}$ and 92.7 % respectively, in the Eden (Fig. 4c). All three catchments exhibited high phosphorus concentrations during the peak of the first event with concentrations and exceedance of 0.89 $\mathrm{mg\,P\,L^{-1}}$ and 0.3 % respectively, in the Hampshire Avon; 0.33 $\mathrm{mg\,P\,L^{-1}}$ and 0.4 % respectively, in the Wensum and 1 $\mathrm{mg\,P\,L^{-1}}$ and 0.003 % respectively, in the Eden DTC. The second event in the Hampshire Avon DTC achieved a similarly high concentration and exceedance (0.97 $\mathrm{mg\,L^{-1}}$ and 0.02 %, respectively), whereas in the Wensum DTC the second event produced a lower concentration and exceedance (0.1 $\mathrm{mg\,L^{-1}}$ and 19.4 %, respectively), indicative of the exhaustion of phosphorus supply after the first event, as discussed below. These data, therefore, 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 shallow, near-surface, overland and deeper throughflow pathways, when compared to conditions observed in each system over the remainder of the hydrological year.

3.2 Hydrograph response

The Hampshire Avon DTC received a total of 88 mm of rainfall during the storm period studied, the highest of all the DTCs, which occurred on the 25–26 April (45 mm) and 29 April (43 mm). This resulted in a small discharge response peaking at 0.34 $\mathrm{m^3\,s^{-1}}$ (0.03 $\mathrm{mm\,h^{-1}}$, 134 % of pre-event discharge), followed by a second larger peak of 1.57 $\mathrm{m^3\,s^{-1}}$ (0.1 $\mathrm{mm\,h^{-1}}$, 361 % of pre-event discharge) on the 29 April (Fig. 5a). The discharge then returned to pre-event levels over the following 2 days. The second discharge peak was larger than the first peak, even though the rainfall totals were similar, which was most probably caused by the difference in antecedent conditions before each event. In the Wensum DTC, the total rainfall between the 25 and 26 of April was 19 mm, which largely fell on the 25 April. This resulted in an increase in discharge at the sub-catchment outlet compared with baseline conditions, which took 10 h to reach a maximum discharge of 1.4 $m^3 s^{-1}$ (0.26 $mm h^{-1}$, 699 % of pre-event discharge), five hours after the period of maximum rainfall intensity of 5 $mm h^{-1}$ (Fig. 5b). This was followed by 20 mm of rain between 27 and 29 April, resulting in a second discharge peak on the 29 April, which took 8.5 h to reach a maximum flow of 0.9 $m^3 s^{-1}$ (0.16 $mm h^{-1}$, 213 % of pre-event discharge), 10.5 h after the period of maximum rainfall intensity of 1.8 $mm h^{-1}$. The Eden DTC received 32.3 mm over the 25–27 April, with 79 % of this rain falling on the 26 April, over a period of 12.75 h, with a maximum intensity of 4.1 $mm h^{-1}$. Time to peak flow was 7.5 h from the start of the event, reaching 3.74 $m^3 s^{-1}$ (0.96 $mm h^{-1}$) approximately 2.75 h after the maximum intensity rainfall (2425 % of pre-event discharge; Fig. 5c). The discharge returned to pre-event conditions 5.5 h after reaching its peak. A small amount of rainfall was also recorded on the 29 of April, but there was no significant response in river discharge.

3.3 Nutrient response

In the Hampshire Avon DTC, the first nutrient to respond to the storm event was nitrate, which showed a dilution in concentration immediately after the rainfall commenced (Fig. 5a). The nitrate concentration fell to 4.5 $mg N L^{-1}$ around the same time as peak flow, before returning to pre-event concentrations of 6.3 $mg N L^{-1}$. The second rainfall event caused another dilution event in nitrate concentration, which occurred as the rainfall commenced, this time with the concentration falling to 2.7 $mg N L^{-1}$ as flow peaked. By contrast, the nitrate concentration in the Wensum DTC (Fig. 5b) at the start of the first event was 6.5 $mg N L^{-1}$. After an initial decrease to 5.5 $mg N L^{-1}$, coinciding with the onset of rainfall, concentrations rose to a maximum of 13.5 $mg N L^{-1}$, five hours after peak discharge. Nitrate showed the longest recovery time of all of the nutrients studied in the Wensum DTC, which after 69 h from peak concentration still had not returned to pre-event concentrations before the onset of the second event. The second event

resulted in a smaller peak with a maximum of 11.6 $mg N L^{-1}$, which occurred 2.5 h after peak discharge. Nitrate did not return to pre-event conditions, due to the onset of another rainfall event on the 1st May.

During both rainfall events in the Hampshire Avon DTC, ammonium responded positively to the increase in flow, showing a steep rising limb from starting concentrations of around 0.1 $mg L^{-1}$ and peaked at the time of maximum event discharge at concentrations of 0.68 and 0.75 $mg L^{-1}$, for events 1 and 2, respectively (Fig. 5a). The ammonium signal had a shallower falling limb, taking around 28 h to return to pre-event concentrations. In the Wensum DTC, ammonium was the first nutrient to show a response to the first rainfall, increasing from a pre-event concentration of 0.2 $mg L^{-1}$ to a maximum of 0.6 $mg L^{-1}$5.5 h later (Fig. 5b). This peak occurred 3 h before the maximum discharge and had the quickest recovery time from the peak concentration to pre-event concentration, of 16.5 h. For the second event, ammonium was again the first nutrient to respond, peaking 3 h before peak discharge, with a recovery time to pre-event concentrations of 7.5 h. Ammonium concentrations at the Eden site were below the limit of detection of 0.1 $mg L^{-1}$ as measured by the ammonium probe.

TP in the Hampshire Avon DTC showed very similar behaviour to that described for ammonium, suggesting that these nutrients originated from similar sources and were mobilised along the same flow pathways in the monitoring period. During both events TP had a steep rising limb, which peaked with discharge and showed a 750 % increase in the first event from pre-event concentrations (0.10–0.89 $mg P L^{-1}$) and around a 600 % increase in the second event (0.18 to > 1 $mg P L^{-1}$, the maximum detection limit of the instrument at the time of this event) (Fig. 5a). Observations of TRP were not available for this storm period in the Hampshire Avon, due to an instrumentation problem. In the Wensum DTC, TP and TRP responded to the rainfall simultaneously during the first event, increasing from 0.06 to a maximum of 0.33 $mg P L^{-1}$ and from 0.04 to a maximum of 0.17 $mg P L^{-1}$, respectively, both peaking one hour before maximum discharge (Fig. 5b). At the point of maximum TP and TRP concentration, TRP constituted 51 % of the measured TP, compared to 74 % at the start of the event. Despite the similar initial response shown by TP and TRP, TP showed the longer recovery time from peak concentration to pre-event concentration of 28 h, compared to 19 h shown by TRP. During the second event TP and TRP concentrations reached a maximum of 0.11 and 0.08 mg P L^{-1}, respectively, both peaking two hours before maximum discharge. Again, TP showed the longer recovery time to pre-event concentrations of 22 h compared to 8 h for TRP. The TP peak of 1 mg P L^{-1} at the Eden site was detected about 0.75 h before the maximum peak flow and 6.75 h from the start of the event (Fig. 5c). TRP concentrations, however, took nearly double the amount of time to reach its peak of 0.21 mg P L^{-1}, reaching maximum concentrations after peak flow. Recovery time from peak to pre-event concentrations was 10.25 and 15.75 h, respectively, for TP and TRP.

Nutrient fluxes were also calculated for each rainfall event, along with total flow volumes (Table 3). For the purposes of this paper, load calculation did not include any estimation of the associated uncertainty, which will be examined in greater depth in future publications. Nitrate-N exports were an order of magnitude higher in the Wensum than the Hampshire Avon DTC, with a loss of over a tonne in each event. The first event in the Wensum had the highest load with an export yield to downstream reaches of 0.69 kg N ha^{-1}. The flow volume of the second event was 74 % of that of the first, and this was reflected in the load, which was also 74 % of that of the first event. Ammonium exports were an order of magnitude higher in the Wensum DTC compared to the Hampshire Avon DTC. TP exports were more comparable between the three catchments, although exports were slightly higher in the Hampshire Avon and Eden compared to the Wensum DTC and the highest export observed was from the second event in the Hampshire Avon. TRP exports were, again, comparable, with very similar export rates in the Wensum and Eden.

3.4 Hysteretic behaviour

The hysteretic behaviour of nitrate, ammonium, TP and TRP, were investigated in each of the events in the Hampshire Avon, Wensum and Eden DTCs (Figs. 6–9). To aid comparison between events and catchments, the hysteresis index, HI$_{\text{mid}}$, 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$_{\text{mid}}$ was then calculated as follows: where $N_{\text{RL}} > N_{\text{FL}}$, HI$_{\text{mid}}$ = (NRL/NFL) – 1, or where $N_{\text{RL}} < N_{\text{FL}}$, HI$_{\text{mid}}$ = (–1/(NRL/NFL)) + 1. The index indicates whether the hysteresis is positive (i.e. clockwise) or negative (i.e. anti-clockwise), and the larger the index, the more hysteretic the relationship between the flow and nutrient (Table 4).

3.4.1 Nitrate

During the first rainfall event, nitrate showed anticlockwise hysteresis in both the Hampshire Avon and Wensum DTCs, but produced very different shaped loops, with a more complex pattern arising in the Hampshire Avon. Although the overall shape of the first hysteresis loop in the Hampshire Avon was anti-clockwise (Fig. 6a), the loop starts in a clockwise direction, followed by a second small and third large anti-clockwise trajectory before completion. The second event (Fig. 6b) produced more of a figure-of-eight shaped loop, switching from anti-clockwise to clockwise twice, and then remaining clockwise for the rest of the loop, hence the positive HI$_{\text{mid}}$ value. These complicated patterns are due to the occurrence of several dilutions in nitrate concentration throughout each event. The first event had five dilutions (Fig. 5a), the first two likely to be associated with the onset of rainfall. However, during the second dilution which occurred on the rising limb of the hydrograph, there was no significant rainfall. The fourth dilution occurred on the falling limb, again with no significant rainfall. 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 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 fourth dilution was followed by a subsequent rise and small peak before the final dilution lead to a recovery of pre-event concentrations, hence the overall anti-clockwise loop. This could represent some flushing of mineral N from the upper soil layers by the activation of sub-surface flow later on in the event. In situations where delayed sub-surface run-off is important, stream water is expected to be initially diluted for some solutes during storm run-off, followed by higher concentrations when the sub-surface component becomes an important contribution (House and Warwick, 1998). 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 $\mathrm{HI}_{\mathrm{mid}}$. The fact that there was no increase in the concentration above pre-event concentrations and, therefore, no anti-clockwise trajectory at the end of the loop for the second event could suggest that the first event was successful in flushing the upper layers of the soil of mineral N, or that the signal may have been masked by the sheer volume of water and the greater influence of event water in the second, larger event.

The anti-clockwise loops in the Wensum DTC indicated substantial transport of nitrate to the stream as opposed to the dilution of baseflow concentrations observed in the Hampshire Avon. For both events, the loops started and ended from the bottom right of the plot (Fig. 6c and d), as opposed to the top left of the plot for the Hampshire Avon. This was due to dilution with the onset of rainfall, followed by a subsequent increase beyond pre-event concentrations. The $\mathrm{HI}_{\mathrm{mid}}$ 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; the smaller flow generated in the second event could explain this lower peak concentration. Other authors have found that shallow groundwater can contribute more nitrate to stream water 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 Wensum DTC. The occurrence of intensive arable agriculture in the Wensum and the use of mineral N fertilisers could have provided the upper soil layers with high concentrations of nitrate-N that is easily mobilised by such events, which has a quick pathway to the stream when there is connectivity of groundwater with upper soil layers via under-drainage.

3.4.2 Ammonium

In the Hampshire Avon DTC, the first storm displayed a figure-of-eight loop for ammonium, which began in the anti-clockwise direction with little response to the initial increase in flow, switched to a clockwise direction on the rising limb and then switched back to anti-clockwise on the falling limb (Fig. 7a), hence the negative $\mathrm{HI}_{\mathrm{mid}}$, due to a long tail on the falling limb. The initial delay in the ammonium response was followed by a sudden increase in concentrations when flow had reached just over $0.2\,\mathrm{m}^3\,\mathrm{s}^{-1}$. This coincided with the third dilution of the nitrate signal at a time when no rainfall was occurring, suggesting the arrival of event water with a relatively short travel time which had mobilised ammonium from near-surface or surface catchment sources. The switch to the anti-clockwise direction on the falling limb suggests that there was a source in the catchment with delayed delivery to the monitoring point. The second event showed similar behaviour, except that the ammonium responded more quickly, although not immediately with rising discharge, and so started in the clockwise direction, peaked shortly before discharge, and then exhibited a long tail, causing a figure-of-eight hysteresis loop as the direction became anti-clockwise near the end of the falling limb (Fig. 7b). Again, the increase in concentrations coincided with the second dilution of the nitrate signal when no rainfall was occurring, implying that this delivery could have been due to the arrival of event water via a sub-surface pathway, which was quicker to respond after the first event. The fact that peak concentrations in the second event occurred before peak flow suggests that this source was becoming exhausted. The anti-clockwise trajectories on the falling limbs of both of these loops in the Hampshire Avon DTC could have been due to the scale of the experimental area ($49.9\,\mathrm{km}^2$); as the near stream sources were becoming exhausted, the delayed delivery of sub-surface ammonium from more distant sources or slower transport pathways in the sub-catchment reached the sampling point on the falling limb. This is likely to be a composite signal of ammonium from a variety of sources including soils, animal manures and farmyard drainage (Holz, 2010; Edwards et al., 2012) as well as sewage, whereby reduced efficiency of sewage treatment works and septic tanks can occur as a result of higher rates of water throughput and reduced residence times leading to elevated ammonium concentrations during periods of high flow (Jarvie et al., 2010; Yates and Johnes, 2013).

Ammonium displayed clockwise hysteresis for both storm events in the Wensum DTC (Fig. 7c and d), with the first storm having a slightly higher HI_{mid} value. Ammonium concentrations peaked around 3.5 h before the peak discharge during both events, which suggests that the source of ammonium must have been either within or close to the river itself, in order for it to be transported and exhausted so rapidly. The source could have potentially been the rainfall and, therefore, the "new water" added to the hydrograph, as exemplified by ammonium concentrations in rainwater in April 2013 measuring over $1\,mg\,N\,L^{-1}$. Alternatively, it could have been derived from livestock waste, as low intensity cattle grazing had commenced in the Wensum catchment at this point for the spring-summer period, creating a small pool of ammonium in surface soils immediately adjacent to the sampling location (Holz, 2010). The second event had a smaller peak concentration and HI_{mid} value, suggesting that exhaustion had begun during the first event. The catchment area monitored by the station in the Wensum was smaller with fewer septic tank inputs than that of the Hampshire Avon which, along with fewer livestock, would explain the lack of ammonium being supplied to the stream on the falling limb. The patterns of ammonium behaviour observed in the Wensum suggest the importance of shallow throughflow, near surface quickflow and overland flow pathways in delivering ammonium to the river, and the lesser importance of lagged deep throughflow in this system, compared to the Hampshire Avon. There is a paucity of studies which demonstrate hysteresis of ammonium during storms and it is, therefore, difficult to compare these findings with wider experience.

3.4.3 Phosphorus

TP showed very similar hysteresis patterns to ammonium in both the Hampshire Avon and the Wensum DTCs for both events. TP in the Hampshire Avon peaked simultaneously with discharge in the first event (Fig. 8a) and then took several hours to return to pre-event conditions. The TP signal also showed an initial delay in response at the beginning of the first event, responding at the same time as ammonium when discharge had exceeded $0.2\,m^3\,s^{-1}$. The loop was very similar in shape to that of ammonium, starting in the clockwise direction and then switching to the anti-clockwise direction on the falling limb. In the second event in the Hampshire Avon DTC, a figure-of-eight loop again occurred, very similar to that of ammonium (Fig. 8b), which was initially clockwise, becoming anti-clockwise on the falling limb. As this TP response mirrored that of ammonium, it is likely that the sub-surface delivery of event water accounted for the initial clockwise hysteretic behaviour, 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; Yates and Johnes, 2013). The fact that TP concentrations in both events reached a concentration of around $1\,mg\,P\,L^{-1}$ suggests that TP was not exhausted from the first event, which had a smaller flow volume, indicating a transport-limited system (Edwards and Withers, 2008).

In the Wensum, TP responded immediately and peaked before the maximum discharge in both events (Fig. 8c and d). In this case, the phosphorus was most likely to originate from remobilised bed-sediment (e.g. Ballantine et al., 2009), field drains and in-wash of phosphorus from the river banks (e.g. Laubel et al., 2000) in response to rainfall and rising river levels (Bowes et al., 2005), while road runoff was also likely to be a source (e.g. 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 Wensum DTC after two events in short succession. TRP behaved in a similar way to TP during both events in the Wensum (Fig. 9a 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, 2007), suggesting that this is source-limited (Edwards and Withers, 2008). 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.

In the Eden, TP showed a weak hysteretic relationship (Fig. 8e) producing a very flat but steep loop. 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 peak discharge, which then quickly returned to pre-event concentrations, with the shape of the TP response mimicking the shape of the hydrograph (Fig. 5c). 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 anti-clockwise 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 ones occurring at the same time as the TP peaks and then a third, peaking after peak discharge (Fig. 9c). This resulted in two initial clockwise loops followed by a large anti-clockwise loop on the falling limb, hence the negative HI_{mid} (Fig. 9c). 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 anti-clockwise 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 became wetted up and slower sub-pathways were activated. The fact that the TP loop was so flat, mimicking the hydrograph, indicates a transport-limited source of P (Edwards and Withers, 2008) as no exhaustion of phosphorus was seen in this event.

4 Discussion

4.1 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, 2012b). The rainfall from April–June in England was nearly three times that for the preceding three months, which has not been experienced in over one hundred years (Marsh and Parry, 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 but previous authors 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). However, there are no documented examples of high temporal resolution data of three different catchments affected by a national-scale drought, where hysteresis has been used to identify the subsequent behaviour of nitrate, ammonium, TP and TRP as the onset of rainfall marked a rapid transition to saturated conditions.

All three DTCs encountered higher than usual rainfall in April 2012, but with discharges making slow recoveries from the dry conditions in March. The weather front that affected the whole country on the 25 April was the first which triggered a discharge response in all three catchments, marking a switch from drought to saturated conditions, with associated connectivity of pollutant transfer pathways from previously dry soils. The extreme flows, along with nitrate and phosphorus concentrations achieved during the events as shown in the duration curves (Fig. 4), demonstrate the impact of these unusual weather patterns within the context of one hydrological year. In the Wensum, the most marked response was that of nitrate, exhibiting fluxes per hectare an order of magnitude higher than those seen in the Hampshire Avon. 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 the crop 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 April 2012. All three catchments exhibited large transfers of phosphorus, with comparable losses per hectare for TP, although slightly higher values were evident for the Hampshire Avon and the Eden DTCs. The first event in the Hampshire Avon, 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. Again, the transport-limited movement of phosphorus in the Eden demonstrated the lack of exhaustion of catchment P sources where this event achieved one of the most extreme responses in the hydrological year, although in contrast to the Hampshire Avon, the particulate fraction made up a large part of the P signal. This finding 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 within the Eden DTC. 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 Wensum DTC, TRP in the Hampshire Avon DTC and particulate P, and therefore sediment, in the Eden DTC. 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.

Understanding the impact of meteorological conditions on catchment water resources and nutrient export are crucial, particularly when such 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. The data presented here demonstrate the consequences during such times of meteorological and hydrological transition, with each catchment highlighting pressures from different pollutants, and their delivery along differing flow pathways as each event evolved.

4.2 The benefits of high frequency water quality monitoring

The benefits of bank-side nutrient analysers have been widely discussed (Jordan et al., 2005, 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 resolution 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 those 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. The hysteresis loops produced here have been extremely valuable for highlighting differences in source-transfer mechanisms both between events in the Hampshire Avon and Wensum DTCs and between all three catchments across the study period. Hysteretic loops for all of the nutrients studied suggest there is a strong sub-surface signal without the presence of under-drainage in the Hampshire Avon that probably reflects deep throughflow and groundwater flow pathways, a strong sub-surface signal with the presence of under-drainage in the Wensum, and a strong overland signal followed by a delayed subsurface signal in the Eden DTC.

An on-going area of research is focusing on the determination of riverine nutrient loads using concentration–discharge relationships where discrete concentration samples are used with higher temporal 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 hydrological 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 the contact time of water with sub-surface materials and 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, and across seasons, and in space, 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 Summary and conclusions

The DTC platforms have been set up as a strategic link between evidence in support of on-farm mitigation measures which reduce pollution of the aquatic environment and formulation of future agri-environmental policy in the UK. The high frequency water quality monitoring infrastructure installed across the three DTCs captured a hydrological transition from drought to flood stress affecting much of the UK. A large weather front moving across the British Isles resulted in the first substantial increase in river discharge in all three catchments at the end of April 2012 following a long dry period. This event produced extreme flows in the context of the hydrological year 2011–2012 with each catchment achieving $< 1\,\%$ exceedance. These substantial discharges resulted in large nutrient transport from the wider sub-catchment to the monitoring point in each DTC. The value of the high resolution monitoring network has been demonstrated by constructing simple hysteresis loops using nutrient concentration and discharge for each DTC, revealing different sources and transport mechanisms in each study area. In the Hampshire Avon, transport was dominated by sub-surface processes, where phosphorus, largely in the soluble form, was found to be transport-limited. In the Wensum DTC, transport was largely dominated by rapid sub-surface movement due to the presence of under-drainage, which mobilised large quantities of nitrate during both events. In the Eden DTC, the transport was found to be initially dominated by surface runoff, which switched to subsurface delivery on the falling limb, with the surface delivery transporting large amounts of particulate phosphorus to the river. The complex hysteresis loops produced form a good basis for further research into catchment processes in the three different landscapes and also highlights the reality of the complex relationship between discharge, concentration and load estimation, where high resolution data, such as those demonstrated here, are essential for improving understanding. The fact that the nutrients studied here showed little sign of exhaustion as a result of high rainfall after the drought period reveals the size of the nutrient pool available in

each catchment, which represents a challenge ahead for environmental managers in militating against agricultural pollution.

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 (EdenDTC, www.edendtc.org.uk) includes Lancaster University, University of Durham, Newcastle University, The Eden Rivers Trust, The Centre for Ecology and Hydrology, The 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, the Game and the 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 and 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.

References

Billen, G., Silvestre, M., Grizzetti, B., Leip, A., Garnier, J., Voss, M., Howarth, R., Bouraoui, F., Lepistö, A., Kortelainen, P., Johnes, P., Curtis, C., Humborg, C., Smedberg, E., Kaste, Ø., Ganeshram, R., Beusen, A., and Lancelot, C.: Nitrogen flows from European regional watersheds, in: The European Nitrogen Assessment: Sources, Effects and Policy Perspectives, edited by: Sutton, M. A., Howard, C. M., Erisman, J. W., Billen, G., Grennfelt, P., van Grinsven, H., and Grizzetti, B., Cambridge University Press, Cambridge, UK, 271–297, 2011.

Boar, R. R., Lister, D. H., and Clough, W. T.: Phosphorus loads in a small groundwater-fed river during the 1989–1992 East Anglian drought, Water Res., 29, 2167–2173, doi:10.1016/0043-1354(95)00034-I, 1995.

Bowes, M. J., House, W. A., Hodgkinson, R. A., and Leach, D. V.: Phosphorus-discharge hysteresis during storm events along a river catchment: the River Swale, UK, Water Res., 39, 751–762, doi:10.1016/j.watres.2004.11.027, 2005.

Burt, T. P., Arkell, B. P., Trudgill, S. T., and Walling, D. E.: Stream nitrate levels in a small catchment in south west England over a period of 15 years (1970–1985), Hydrol. Process., 2, 267–284, doi:10.1002/hyp.3360020307, 1988.

Cherry, K. A., Shepherd, M., Withers, P. J. A., and Mooney, S. J.: Assessing the effectiveness of actions to mitigate nutrient loss from agriculture: a review of methods, Sci. Total Environ., 406, 1–23, doi:10.1016/j.scitotenv.2008.07.015, 2008.

Collins, A., Ohandja, D. G., Hoare, D., and Voulvoulis, N.: Implementing the water framework directive: a transition from established monitoring networks in England and Wales, Environ. Sci. Policy, 17, 49–61, doi:10.1016/j.envsci.2011.11.003, 2012.

Dean, S., Freer, J., Beven, K., Wade, A., and Butterfield, D.: Uncertainty assessment of a process-based integrated catchment model of phosphorus, Stoch. Env. Res. Risk A., 23, 991–1010, doi:10.1007/s00477-008-0273-z, 2009.

Defra: Guidelines on the Use of Scientific Analysis in Policy Making, Defra, London, 2005.

Drewry, J. J., Newham, L. T. H., and Croke, B. F. W.: Suspended sediment, nitrogen and phosphorus concentrations and exports during storm-events to the Tuross estuary, Australia, J. Environ. Manage., 90, 879–887, doi:10.1016/j.jenvman.2008.02.004, 2009.

Dworak, T., Gonzalez, C., Laaser, C., and Interwies, E.: The need for new monitoring tools to implement the WFD, Environ. Sci. Policy, 8, 301–306, doi:10.1016/j.envsci.2005.03.007, 2005.

EA: available at: http://www.environment-agency.gov.uk/research/planning/40313.aspx, last access: 13 January 2013.

Eden, P.: April 2012, cold and exceptionally wet; notable shortage of sunshine in the east and northeast, Weather, 67, i–iv, doi:10.1002/wea.1862, 2012.

Eder, A., Strauss, P., Krueger, T., and Quinton, J. N.: Comparative calculation of suspended sediment loads with respect to hysteresis effects (in the Petzenkirchen catchment, Austria), J. Hydrol., 389, 168–176, doi:10.1016/j.jhydrol.2010.05.043, 2010.

Edwards, A. C. and Withers, P. J. A.: Transport and delivery of suspended solids, nitrogen and phosphorus from various sources to freshwaters in the UK, J. Hydrol., 350, 144–153, doi:10.1016/j.jhydrol.2007.10.053, 2008.

Edwards, A. C., Watson, H. A., and Cook, Y. E. M.: Source strengths, transport pathways and delivery mechanisms of nutrients, suspended solids and coliforms within a small agricultural headwater catchment, Sci. Total Environ., 434, 123–129, doi:10.1016/j.scitotenv.2011.10.055, 2012.

Evans, D. J. and Johnes, P. J.: Physico-chemical controls on phosphorus cycling in two lowland streams – Part 1: The water column, Sci. Total Environ., 329, 145–163, 2004.

Foster, I. D. L. and Walling, D. E.: The effects of the 1976 drought and autumn rainfall on stream solute levels, Earth Surf. Proc., 3, 393–406, doi:10.1002/esp.3290030407, 1978.

Gooddy, D. C., Darling, W. G., Abesser, C., and Lapworth, D. J.: Using chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF6) to characterise groundwater movement and residence time in a lowland Chalk catchment, J. Hydrol., 330, 44–52, doi:10.1016/j.jhydrol.2006.04.011, 2006.

Grizzetti, B., Bouraoui, F., Billen, G., van Grinsven, H., Cardoso, A. C., Thieu, V., Garnier, J., Curtis, C., Howarth, R. W., and Johnes, P. J: Nitrogen as a threat to European water quality, in: European Nitrogen Assessment, edited by: Sutton, M. A., Howard, C. M., Erisman, J. W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H., and Grizzetti, B., Cambridge University Press, Cambridge, UK, 379–404, 2011.

Haygarth, P. M., Warwick, M. S., and House, W. A.: Size distribution of colloidal molybdate reactive phosphorus in river waters and soil solution, Water Res., 31, 439–448, doi:10.1016/S0043-1354(96)00270-9, 1997.

Haygarth, P. M., Wood, F. L., Heathwaite, A. L., and Butler, P. J.: Phosphorus dynamics observed through increasing scales in a nested headwater-to-river channel study, Sci. Total Environ., 344, 83–106, 2005.

Haygarth, P. M., Page, T. J. C., Beven, K. J., Freer, J., Joynes, A., Butler, P., Wood, G. A., and Owens, P. N.: Scaling up the phosphorus signal from soil hillslopes to headwater catchments, Freshwater Biol., 57, 7–25, doi:10.1111/j.1365-2427.2012.02748.x, 2012.

Healthy Waterways: available at: http://www.healthywaterways.org/Home.aspx, last access: 13 January 2013.

Heathwaite, L., Haygarth, P., Matthews, R., Preedy, N., and Butler, P.: Evaluating colloidal phosphorus delivery to surface waters from diffuse agricultural sources, J. Environ. Qual., 34, 287–298, doi:10.2134/jeq2005.0287, 2005.

Hively, W. D., Bryant, R. B., and Fahey, T. J.: Phosphorus concentrations in overland flow from diverse locations on a New York dairy farm, J. Environ. Qual., 34, 1224–1233, doi:10.2134/jeq2004.0116, 2005.

Holz, G. K.: Sources and processes of contaminant loss from an intensively grazed catchment inferred from patterns in discharge and concentration of thirteen analytes using high intensity sampling, J. Hydrol., 383, 194–208, doi:10.1016/j.jhydrol.2009.12.036, 2010.

House, W. A. and Warwick, M. S.: Hysteresis of the solute concentration/discharge relationship in rivers during storms, Water Res., 32, 2279–2290, doi:10.1016/S0043-1354(97)00473-9, 1998.

Jackson, B. M., Wheater, H. S., Mathias, S. A., McIntyre, N., and Butler, A. P.: A simple model of variable residence time flow and nutrient transport in the chalk, J. Hydrol., 330, 221–234, doi:10.1016/j.jhydrol.2006.04.045, 2006.

Jarvie, H. P., Neal, C., Williams, R. J., Neal, M., Wickham, H. D., Hill, L. K., Wade, A. J., Warwick, A., and White, J.: Phosphorus sources, speciation and dynamics in the lowland eutrophic River Kennet, UK, Sci. Total Environ., 282–283, 175–203, doi:10.1016/S0048-9697(01)00951-2, 2002.

Jarvie, H. P., Neal, C., and Withers, P. J. A.: Sewage-effluent phosphorus: a greater risk to river eutrophication than agricultural phosphorus?, Sci. Total Environ., 360, 246–253, doi:10.1016/j.scitotenv.2005.08.038, 2006.

Jarvie, H. P., Withers, P. J. A., Hodgkinson, R., Bates, A., Neal, M., Wickham, H. D., Harman, S. A., and Armstrong, L.: Influence of rural land use on streamwater nutrients and their ecological significance, J. Hydrol., 350, 166–186, doi:10.1016/j.jhydrol.2007.10.042, 2008.

Jarvie, H. P., Withers, P. J. A., Bowes, M. J., Palmer-Felgate, E. J., Harper, D. M., Wasiak, K., Wasiak, P., Hodgkinson, R. A., Bates, A., Stoate, C., Neal, M., Wickham, H. D., Harman, S. A., and Armstrong, L. K.: Streamwater phosphorus and nitrogen across a gradient in rural–agricultural land use intensity, Agr. Ecosyst. Environ., 135, 238–252, doi:10.1016/j.agee.2009.10.002, 2010.

Johnes, P. J.: Meeting ecological restoration targets in European Waters: a challenge for animal agriculture, in: Redesigning Animal Agriculture: The Challenge for the 21st Century, edited by: SSwain, D. L., Charmley, E., Steel, J., and Coffey, S., CAB International, Wallingford, 185–203, 2007a.

Johnes, P. J.: Uncertainties in annual riverine phosphorus load estimation: impact of load estimation methodology, sampling frequency, baseflow index and catchment population density, J. Hydrol., 332, 241–258, doi:10.1016/j.jhydrol.2006.07.006, 2007b.

Johnes, P. J. and Hodgkinson, R. A.: Phosphorus loss from agricultural catchments: pathways and implications for management, Soil Use Manage., 14, 175–185, doi:10.1111/j.1475-2743.1998.tb00637.x, 1998.

Jordan, P. and Cassidy, R.: Technical Note: Assessing a 24/7 solution for monitoring water quality loads in small river catchments, Hydrol. Earth Syst. Sci., 15, 3093–3100, doi:10.5194/hess-15-3093-2011, 2011.

Jordan, P., Arnscheidt, A., McGrogan, H., and McCormick, S.: Characterising phosphorus transfers in rural catchments using a continuous bank-side analyser, Hydrol. Earth Syst. Sci., 11, 372–381, doi:10.5194/hess-11-372-2007, 2007.

Jordan, P., Arnscheidt, J., McGrogan, H., and McCormick, S.: High-resolution phosphorus transfers at the catchment scale: the hidden importance of non-storm transfers, Hydrol. Earth Syst. Sci., 9, 685–691, doi:10.5194/hess-9-685-2005, 2005.

Jose, P.: Long-term nitrate trends in the river trent and four major tributaries, Regul. River, 4, 43–57, doi:10.1002/rrr.3450040105, 1989.

Kirchner, J. W., Feng, X. H., Neal, C., and Robson, A. J.: The fine structure of water-quality dynamics: the (high-frequency) wave of the future, Hydrol. Process., 18, 1353–1359, doi:10.1002/Hyp.5537, 2004.

Lawler, D. M., Petts, G. E., Foster, I. D. L., and Harper, S.: Turbidity dynamics during spring storm events in an urban headwater river system: the Upper Tame, West Midlands, UK, Sci. Total Environ., 360, 109–126, doi:10.1016/j.scitotenv.2005.08.032, 2006.

Leip, A., Achermann, B., Billen, G., Bleeker, A., Bouwman, A., de Vries, W., Dragosits, U., Doring, U., Fernall, D., Geupel, M., Herolstab, J., Johnes, P. J., Le Gall, A. C., Monni, S., Neveceral, R., Orlandini, L., Prud'homme, M., Reuter, H., Simpson, D., Seufert, G., Spranger, T., Sutton, M., van Aardenne, J., Voss, M., and Winiwarter, W: Integrating nitrogen fluxes at the European scale, in: European Nitrogen Assessment, edited by: Sutton, M. A., Howard, C. M., Erisman, J. W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H., and Grizzetti, B., Cambridge University Press, Cambridge, UK, 345–376, 2011.

Liefferink, D., Wiering, M., and Uitenboogaart, Y.: The EU water framework directive: a multi-dimensional analysis of implementation and domestic impact, Land Use Policy, 28, 712–722, doi:10.1016/j.landusepol.2010.12.006, 2011.

LWEC: Demonstration Test Catchments: available at: http://www.lwec.org.uk/activities/demonstration-test-catchments, last access: 13 January 2013.

Marsh, T. and Parry, S.: Hydrological summary for the United Kingdom: April 2012, NERC/Centre for Ecology & Hydrology, Wallingford, UK, 2012a.

Marsh, T. and Parry, S.: An overview of the 2010–12 drought and its dramatic termination, NERC/Centre for Ecology & Hydrology, Wallingford, UK, 2012b.

McDonnell, J. J., Sivapalan, M., Vaché, K., Dunn, S., Grant, G., Haggerty, R., Hinz, C., Hooper, R., Kirchner, J., Roderick, M. L., Selker, J., and Weiler, M.: Moving beyond heterogeneity and process complexity: a new vision for watershed hydrology, Water Resour. Res., 43, W07301, doi:10.1029/2006WR005467, 2007.

McGlynn, B., McDonnell, J., Stewart, M., and Seibert, J.: On the relationships between catchment scale and streamwater mean residence time, Hydrol. Process., 17, 175–181, doi:10.1002/hyp.5085, 2003.

McGuire, K. J., McDonnell, J. J., Weiler, M., Kendall, C., McGlynn, B. L., Welker, J. M., and Seibert, J.: The role of topography on catchment-scale water residence time, Water Resour. Res., 41, W05002, doi:10.1029/2004WR003657, 2005.

McMillan, H., Krueger, T., and Freer, J.: Benchmarking observational uncertainties for hydrology: rainfall, river discharge and water quality, Hydrol. Process., 26, 4078–4111, doi:10.1002/hyp.9384, 2012.

Moliere, D. R., Evans, K. G., Saynor, M. J., and Erskine, W. D.: Estimation of suspended sediment loads in a seasonal stream in the wet-dry tropics, Northern Territory, Australia, Hydrol. Process., 18, 531–544, doi:10.1002/hyp.1336, 2004.

NCEP: available at: http://polar.ncep.noaa.gov/sst/oper/Welcome.html, last access: 13 January 2013.

O'Connor, E. M., McConnell, C., Lembcke, D., and Winter, J. G.: Estimation of total phosphorus loads for a large, flashy river of a highly developed watershed–seasonal and hysteresis effects, J. Great Lakes Res., 37, 26–35, doi:10.1016/j.jglr.2011.04.004, 2011.

Oeurng, C., Sauvage, S., and Sanchez-Perez, J. M.: Temporal variability of nitrate transport through hydrological response during flood events within a large agricultural catchment in south-west France, Sci. Total Environ., 409, 140–149, doi:10.1016/j.scitotenv.2010.09.006, 2010.

Owen, G. J., Perks, M. T., Benskin, C. M. H., Wilkinson, M. E., Jonczyk, J., and Quinn, P. F.: Monitoring agricultural diffuse pollution through a dense monitoring network in the River Eden Demonstration Test Catchment, Cumbria, UK, Area, 44, 443–453, doi:10.1111/j.1475-4762.2012.01107.x, 2012.

Palmer-Felgate, E. J., Jarvie, H. P., Williams, R. J., Mortimer, R. J. G., Loewenthal, M., and Neal, C.: Phosphorus dynamics and productivity in a sewage-impacted lowland chalk stream, J. Hydrol., 351, 87–97, doi:10.1016/j.jhydrol.2007.11.036, 2008.

Robson, A. and Reed, D.: Flood estimation handbook – FEH CD-ROM 3, Institute of Hydrology, Wallingford, 1999.

Rozemeijer, J. C. and Broers, H. P.: The groundwater contribution to surface water contamination in a region with intensive agricultural land use (Noord-Brabant, the Netherlands), Environ. Pollut., 148, 695–706, doi:10.1016/j.envpol.2007.01.028, 2007.

Scholefield, D., Le Goff, T., Braven, J., Ebdon, L., Long, T., and Butler, M.: Concerted diurnal patterns in riverine nutrient concentrations and physical conditions, Sci. Total Environ., 344, 201–210, doi:10.1016/j.scitotenv.2005.02.014, 2005.

Skamarock, W. C. and Klemp, J. B.: A time-split nonhydrostatic atmospheric model for weather research and forecasting applications, J. Comput. Phys., 227, 3465–3485, doi:10.1016/j.jcp.2007.01.037, 2008.

Teagasc, Agricultural Catchments Programme: available at: http://www.teagasc.ie/agcatchments/, last access: 13 January 2013.

Wade, A. J., Palmer-Felgate, E. J., Halliday, S. J., Skeffington, R. A., Loewenthal, M., Jarvie, H. P., Bowes, M. J., Greenway, G. M., Haswell, S. J., Bell, I. M., Joly, E., Fallatah, A., Neal, C., Williams, R. J., Gozzard, E., and Newman, J. R.: Hydrochemical processes in lowland rivers: insights from in situ, high-resolution monitoring, Hydrol. Earth Syst. Sci., 16, 4323–4342, doi:10.5194/hess-16-4323-2012, 2012.

Weiler, M., McGlynn, B. L., McGuire, K. J., and McDonnell, J. J.: How does rainfall become runoff? A combined tracer and runoff transfer function approach, Water Resour. Res., 39, 1315, doi:10.1029/2003WR002331, 2003.

Withers, P. J. A. and Lord, E. I.: Agricultural nutrient inputs to rivers and groundwaters in the UK: policy, environmental management and research needs, Sci. Total Environ., 282–283, 9–24, 2002.

Withers, P. J. A., Jarvie, H. P., Hodgkinson, R. A., Palmer-Felgate, E. J., Bates, A., Neal, M., Howells, R., Withers, C. M., and Wickham, H. D.: Characterization of phosphorus sources in rural watersheds, J. Environ. Qual., 38, 1998–2011, doi:10.2134/jeq2008.0096, 2009.

Woods, R. and Sivapalan, M.: A synthesis of space-time variability in storm response: Rainfall, runoff generation, and routing, Water Resour. Res., 35, 2469–2485, doi:10.1029/1999WR900014, 1999.

Yates, C. A. and Johnes, P. J.: Nitrogen speciation and phosphorus fractionation dynamics in a lowland Chalk catchment, Sci. Total Environ., 444, 466–479, doi:10.1016/j.scitotenv.2012.12.002, 2013.

Table 1. Summary characteristics for the Hampshire Avon, Wensum and Eden DTCs.

	Hampshire Avon	Wensum	Eden
Sub-catchment	Wylye at Brixton Deverill	Blackwater Drain at Park Farm	Morland at Newby Beck
Sampling location (BNG)	ST 868 401	TG 125 246	NY 600 213
Size of catchment (km^2)	50.2	19.7	12.5
Elevation (m a.s.l.)	189*	43*	233*
Aspect (° from north)	106*	144*	28*
Geology/soils	Cretaceous Chalk and Greensand	Quaternary glacial sands and gravels over till/clay loam over Cretaceous Chalk	Glacial till over Carboniferous limestone
Annual average rainfall (mm)	886–909*	655*	1167*
Baseflow index (BFI)	0.93*	0.80*	0.39*
Landuse	Livestock and cereals	Arable crops	Livestock

* Taken from (Robson and Reed, 1999).
BNG: British National Grid.

Table 2. Storm event rainfall characteristics in each DTC.

	Hampshire Avon		Wensum		Eden
	Event 1	Event 2	Event 1	Event 2	Event 1
Date (2012)	25–26 Apr	29 Apr	25–26 Apr	27–29 Apr	26–27 Apr
Total rainfall (mm)	45	43	19	20	32
Max intensity (mm h^{-1})	*	*	5	1.8	4.1

* Data not available in the Hampshire Avon during the storm event.

Table 3. Nutrient fluxes for each storm event in the Hampshire Avon, Wensum and Eden DTCs as absolute load and export.

DTC	Event	Total flow volume (m^3)	NO_3-N		NH_4-N		TP		TRP	
			Load (kg N)	Export (kg N ha^{-1})	Load (kg N)	Export (kg N ha^{-1})	Load (kg P)	Export (kg P ha^{-1})	Load (kg P)	Export (kg P ha^{-1})
Hampshire Avon	1	24 437 (0.44 mm)	90	0.018	2	0.0004	13	0.003	–	–
	2	90 275 (1.6 mm)	359	0.075	37	0.007	56	0.011	–	–
Wensum	1	134 430 (6.8 mm)	1364	0.692	37	0.019	14	0.007	8	0.004
	2	96 506 (4.9 mm)	1005	0.510	24	0.012	6	0.003	4	0.002
Eden	1	230 846 (16.5 mm)	–	–	–	–	13	0.009	5	0.004

Table 4. Summary of estimated values of the hysteresis index, HI_{mid}, for each nutrient peak in the Hampshire Avon, Wensum and Eden DTCs.

DTC	Event	NO_3-N	NH_4-N	TP	TRP
Hampshire Avon	1	−0.18	−4.28	−3.16	–
	2	0.11	0.64	0.19	–
Wensum	1	−1.08	0.92	2.25	2.4
	2	−0.43	0.72	0.48	0.63
Eden	1	–	–	−0.02	−0.82

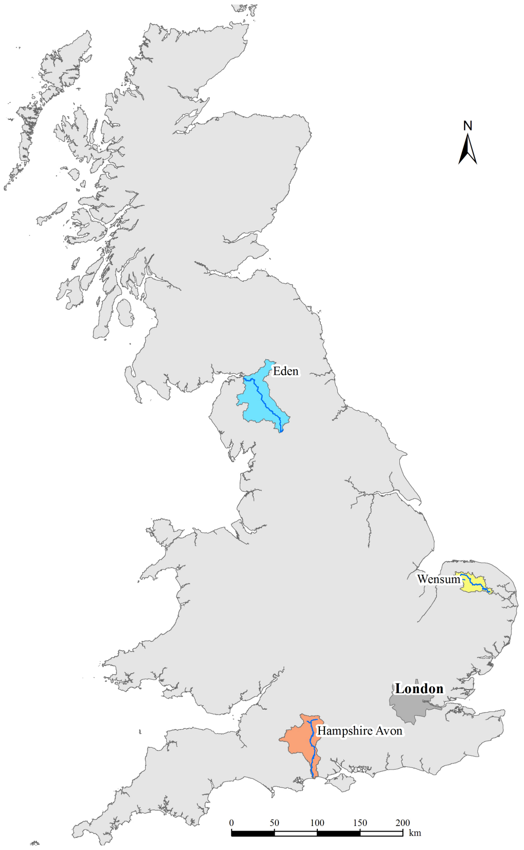

Fig. 1. Location map of England showing the three Defra Demonstration Test Catchments.

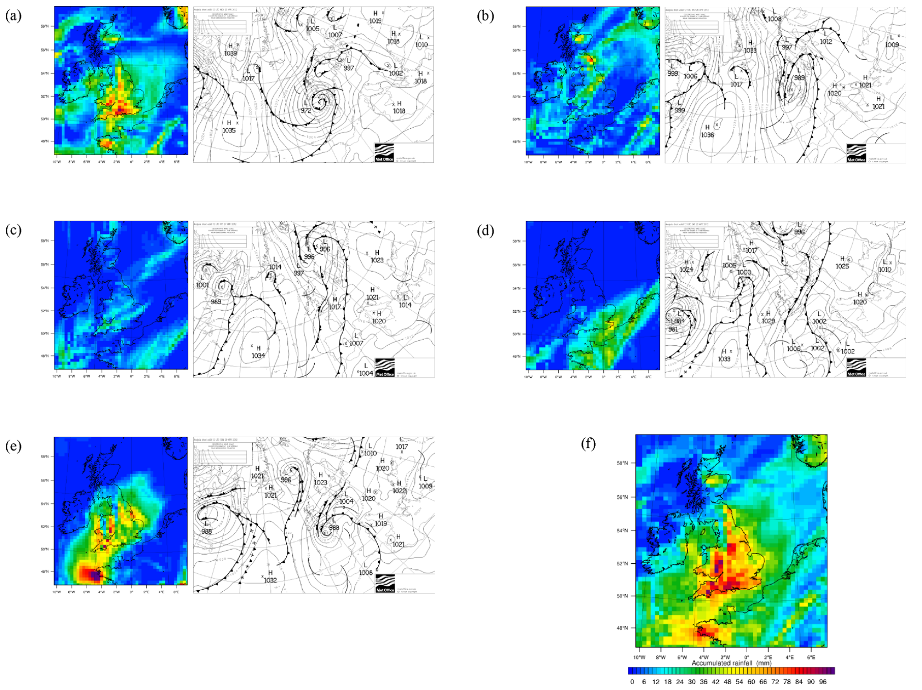

Fig. 2. 12:00 UTC daily rainfall totals (left panels) and Sea Level Pressure Chart (right panels) modelled using the Weather Research and Forecasting ARW model for **(a)** 25 April **(b)** 26 April **(c)** 27 April **(d)** 28 April **(e)** 29 April and **(f)** 5 day rainfall total for period 25–29 April 2012.

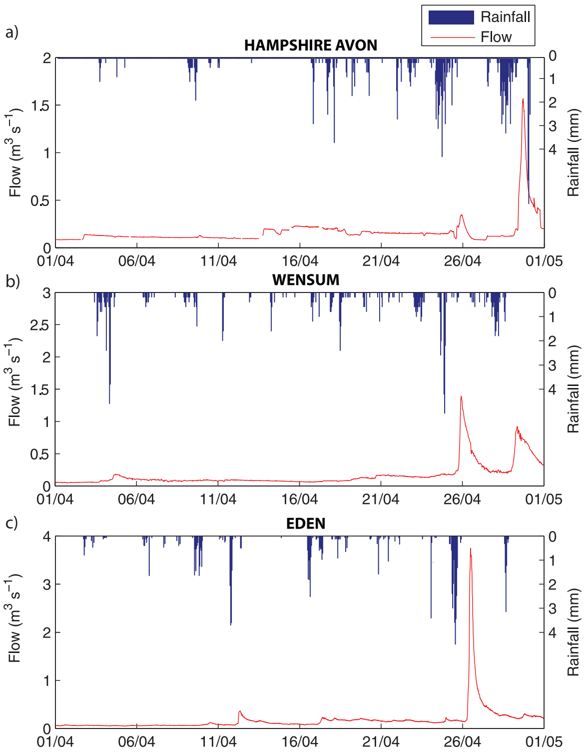

Fig. 3. Plots showing rainfall (mm) and flow ($m^3 s^{-1}$) during April 2012 in the **(a)** Hampshire Avon **(b)** Eden and **(c)** Wensum DTCs.

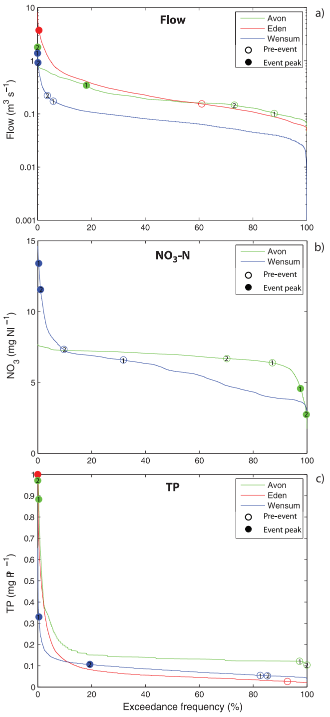

Fig. 4. Exceedance plots for **(a)** flow **(b)** nitrate and **(c)** TP in the Hampshire Avon, Eden and Wensum DTCs. Open circles illustrate pre-event values and filled circles illustrate peak-event values. Two storm events are recorded in the Hampshire Avon and the Wensum, numbered 1 and 2, with 1 being from 25–29 April and 2 being from 29–30 April 2012.

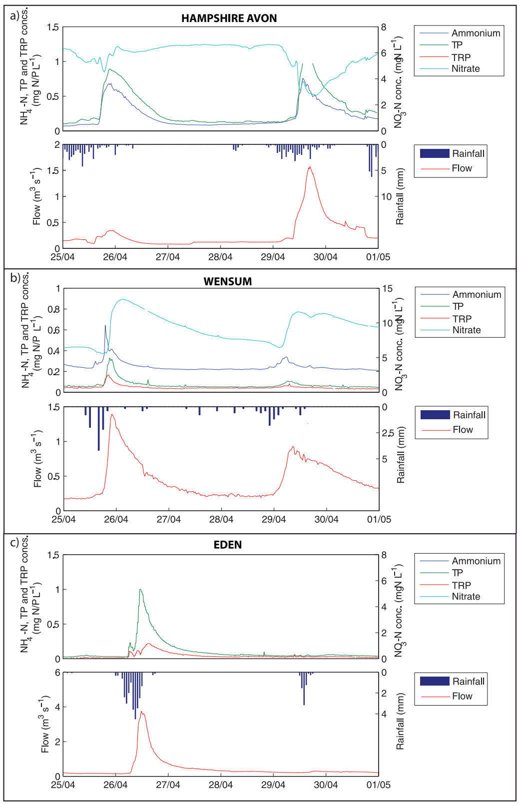

Fig. 5. Plots showing nutrient response to rainfall and flow events in **(a)** the Hampshire Avon **(b)** Eden and **(c)** Wensum DTCs.

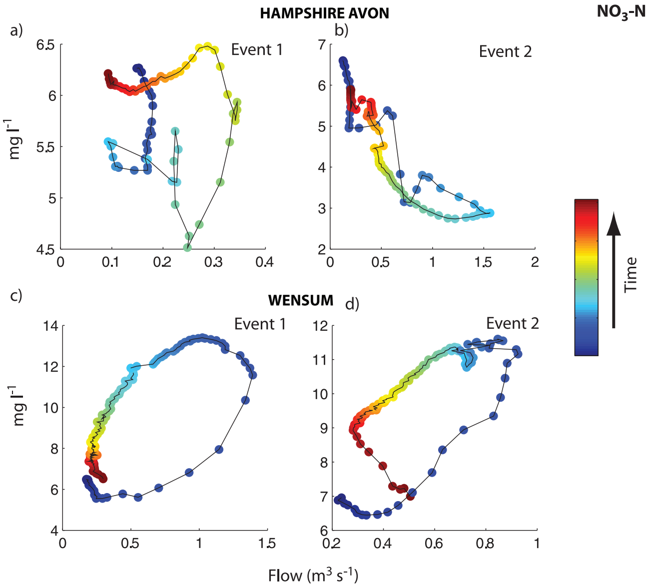

Fig. 6. Plots showing hysteretic behaviour in nitrate during storm events in (**a** and **b**) the Hampshire Avon and (**c** and **d**) Wensum DTCs.

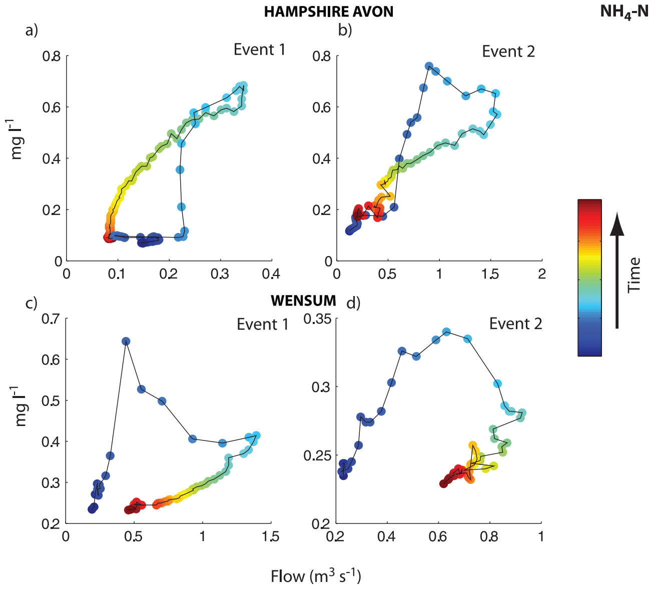

Fig. 7. Plots showing hysteretic behaviour in ammonium during storm events in (**a** and **b**) the Hampshire Avon and (**c** and **d**) Wensum DTCs.

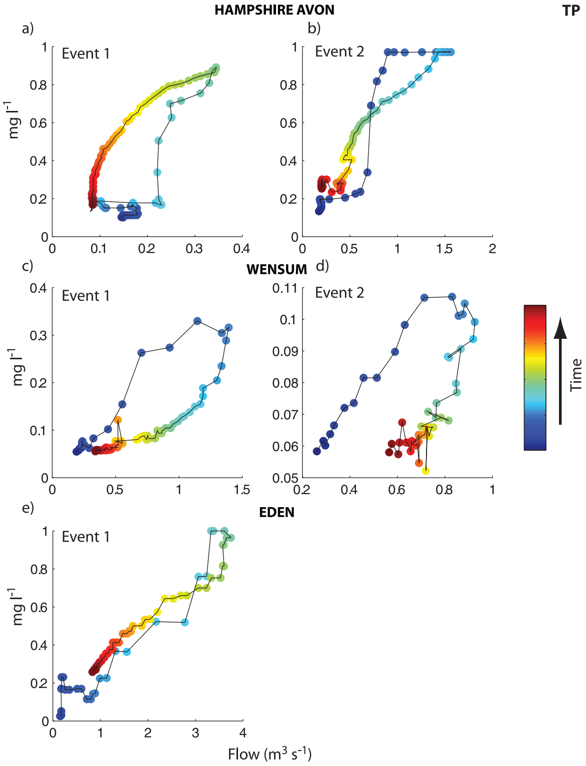

Fig. 8. Plots showing hysteretic behaviour in TP during storm events in (**a** and **b**) the Hampshire Avon (**c** and **d**) Wensum and **(e)** Eden DTCs.

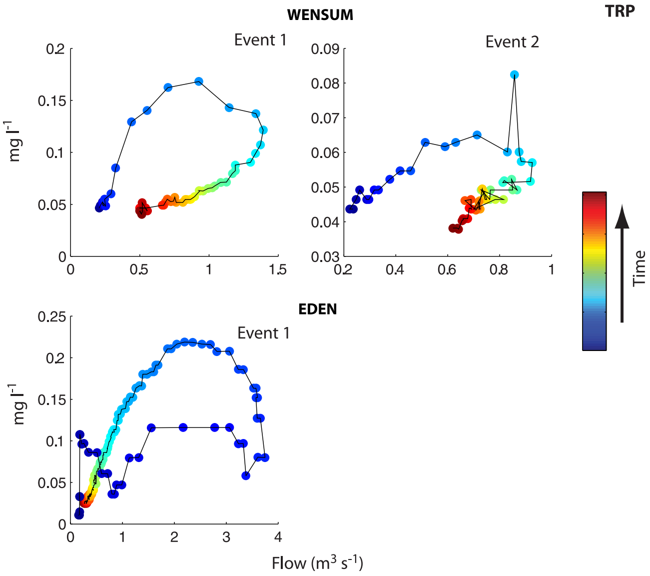

Fig. 9. Plots showing hysteretic behaviour in TRP during storm events in (**a** and **b**) the Wensum and **(c)** Eden DTCs.