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Changing climate and nutrient transfers: Evidence from high temporal resolution concentration-flow dynamics in headwater catchments

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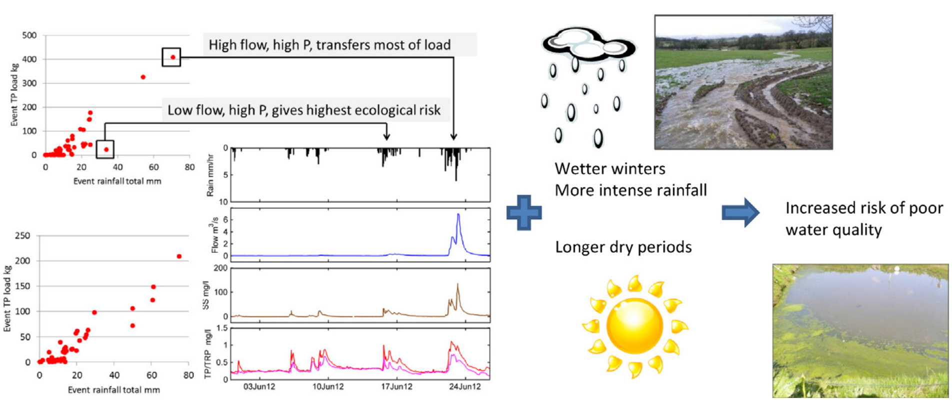
HIGHLIGHTS

- Climate change may increase pollutant transfers from agricultural land.
- High temporal resolution data enabled present day nutrient dynamics to be analysed.
- High flow events (>Q10) transported >90% of sediment, >80% of phosphorus
- Longer periods of low flow and high concentration will increase ecological risk.
- Average phosphorus loads may increase by 9% with higher rainfall volume and intensity.

GRAPHICAL ABSTRACT



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ABSTRACT

We hypothesise that climate change, together with intensive agricultural systems, will increase the transfer of pollutants from land to water and impact on stream health. This study builds, for the first time, an integrated assessment of nutrient transfers, bringing together a) high-frequency data from the outlets of two surface water-dominated, headwater (~10 km^2) agricultural catchments, b) event-by-event analysis of nutrient transfers, c) concentration duration curves for comparison with EU Water Framework Directive water quality targets, d) event analysis of location-specific, sub-daily rainfall projections (UKCP, 2009), and e) a linear model relating storm rainfall to phosphorus load. These components, in combination, bring innovation and new insight into

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the estimation of future phosphorus transfers, which was not available from individual components. The data demonstrated two features of particular concern for climate change impacts. Firstly, the bulk of the suspended sediment and total phosphorus (TP) load (greater than 90% and 80% respectively) was transferred during the highest discharge events. The linear model of rainfall-driven TP transfers estimated that, with the projected increase in winter rainfall (+8% to +17% in the catchments by 2050s), annual event loads might increase by around 9% on average, if agricultural practices remain unchanged. Secondly, events following dry periods of several weeks, particularly in summer, were responsible for high concentrations of phosphorus, but relatively low loads. The high concentrations, associated with low flow, could become more frequent or last longer in the future, with a corresponding increase in the length of time that threshold concentrations (e.g. for water quality status) are exceeded. The results suggest that in order to build resilience in stream health and help mitigate potential increases in diffuse agricultural water pollution due to climate change, land management practices should target controllable risk factors, such as soil nutrient status, soil condition and crop cover.
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1. Introduction

Freshwater systems throughout the world provide many essential services to the global population. There are multiple stressors on this valuable resource (Heathwaite, 2010), including those on both water quantity (Vorosmarty et al., 2000) and quality (Onda et al., 2012; Seitzinger et al., 2010). In the future, these pressures will continue to increase, with larger populations making greater demands for food production, and, consequently, more intensive farming practices. The pressures are further exacerbated by the effect of a changing climate, which is predicted to bring more frequent extreme events (Kendon et al., 2014; Murphy et al., 2009), resulting in the likelihood of more winter runoff and longer periods of low flow (Bell et al., 2012; Wilby et al., 2006), although still with much uncertainty (Arnell, 2011; Kay and Jones, 2012; Prudhomme et al., 2012). In conjunction with projected climatic changes, previous studies have indicated likely increases in sediment and nutrient loads (Crossman et al., 2014; El-Khoury et al., 2015; Jeppesen et al., 2009; Jeppesen et al., 2011; Macleod et al., 2012; Rankinen et al., 2015; Whitehead et al., 2009).

In Europe, the Water Framework Directive (WFD) (2000/60/EC: European Union, 2000) continues to drive the requirement to meet national-level water quality targets in individual water bodies (rivers and lakes). Despite this, in England, 73% of water bodies fail to meet good ecological status (Defra et al., 2015), and many of the condition assessments cite 'diffuse water pollution from agriculture', especially agricultural losses of phosphorus (P) and nitrogen (N), as key pressures.

The response of a surface water catchment (in temperate areas) to rainfall is dominated by the processes in the headwater sub-catchments comprising the network of first and second order streams (Strahler order). These first and second order streams make up most of the channel length and basin area of a larger catchment (Burt, 1997), and contribute at least 60–70% of the water (Alexander et al., 2007; Decamps et al., 1999). Many researchers (e.g. Harris and Heathwaite, 2005; Heathwaite, 2010; Johnes, 2007; Jordan et al., 2005a) have identified the need for small scale and short timestep data in order to unravel the complex processes of nutrient cycling in headwaters. Headwater catchments are very dynamic and their responses may be misrepresented by infrequent, low intensity sampling regimes (Cassidy and Jordan, 2011; Defew et al., 2013).

Hydrological event or campaign focussed sampling, particularly in short-term research studies, has demonstrated the importance of high resolution monitoring and of rainfall-driven events in the transfer of diffuse pollution from agriculture (e.g. Bilotta et al., 2008; Deasy et al., 2008; Haygarth et al., 2006; Haygarth et al., 2012; Heathwaite and Dils, 2000; Preedy et al., 2001; Sharpley et al., 2001), with the phytobenthic community suggesting a direct impact on water quality (Snell et al., 2014). However, for many water bodies, the only available water quality data are the standard condition assessments and the Environment Agency national level programme of routine monitoring at main river (large catchment scale) locations, at fortnightly or monthly resolution. These can provide valuable information for the identification of sites that are under pressure, but do not capture the high frequency dynamics of the system. The problems associated with infrequent sampling are well documented (e.g. Cassidy and Jordan, 2011) and can lead to large uncertainty in annual load calculations of sediment and nutrients (Defew et al., 2013). There is, therefore, increasing interest in the use of in-stream high resolution water quality monitoring to assemble higher resolution catchment-scale datasets (e.g. Bowes et al., 2015; Halliday et al., 2012; Jordan et al., 2012; Melland et al., 2012; Mellander et al., 2012; Mellander et al., 2014; Outram et al., 2014; Skeffington et al., 2015; Wade et al., 2012), which can be used to understand key catchment processes in terms of hydrology, diffuse pollution transfer and trophic impacts and how these may alter under a changing climate.

For much of the UK, climate change is expected to bring warmer, wetter winters, with fewer but more intense rain days, and hotter, drier summers (Murphy et al., 2009) and an increase in extreme events, including summer storms (Kendon et al., 2014). We hypothesise that climate change will alter the transfer of nutrients from land to water, and this study makes an integrated assessment of nutrient transfers, bringing together, for the first time:

- high-frequency data from the outlets of two surface water-dominated, headwater (~10 km^2) agricultural catchments within the River Eden catchment, Cumbria, UK
- event-by-event analysis of suspended sediment (SS), total phosphorus (TP), total reactive phosphorus (TRP) and nitrate (NO_3^-) transfers
- concentration duration curves for each season for comparison with EU Water Framework Directive water quality targets
- event analysis of location-specific, sub-daily rainfall projections (UKCP, 2009)
- a linear model relating storm rainfall to phosphorus load

The unique combination of these components brings new insight into the estimation of future phosphorus transfers, which was not available from individual components.

2. Materials and methods

2.1. Site description

The field dataset was generated as part of the Demonstration Test Catchments (DTC) programme (McGonigle et al., 2014). Newby Beck (12.5 km^2) and Pow Beck (10.5 km^2) are two rural headwater catchments within the Eden river catchment, in Cumbria, UK (Fig. 1). Newby Beck Fig. 1b) is generally steeper (23% of catchment area steeper than 5°) and at higher altitude (range 150–345 m above sea level) than Pow Beck (<1% steeper than 5°; altitude 60–155 m, (Fig. 1c)).

The bedrock of the larger Eden catchment comprises Permian and Triassic sandstones in the valley bottom, overlying rocks of the Carboniferous Series. The valley sides are mainly Carboniferous limestone and limestone/mudstone layers (Fig. 2). The sandstones are

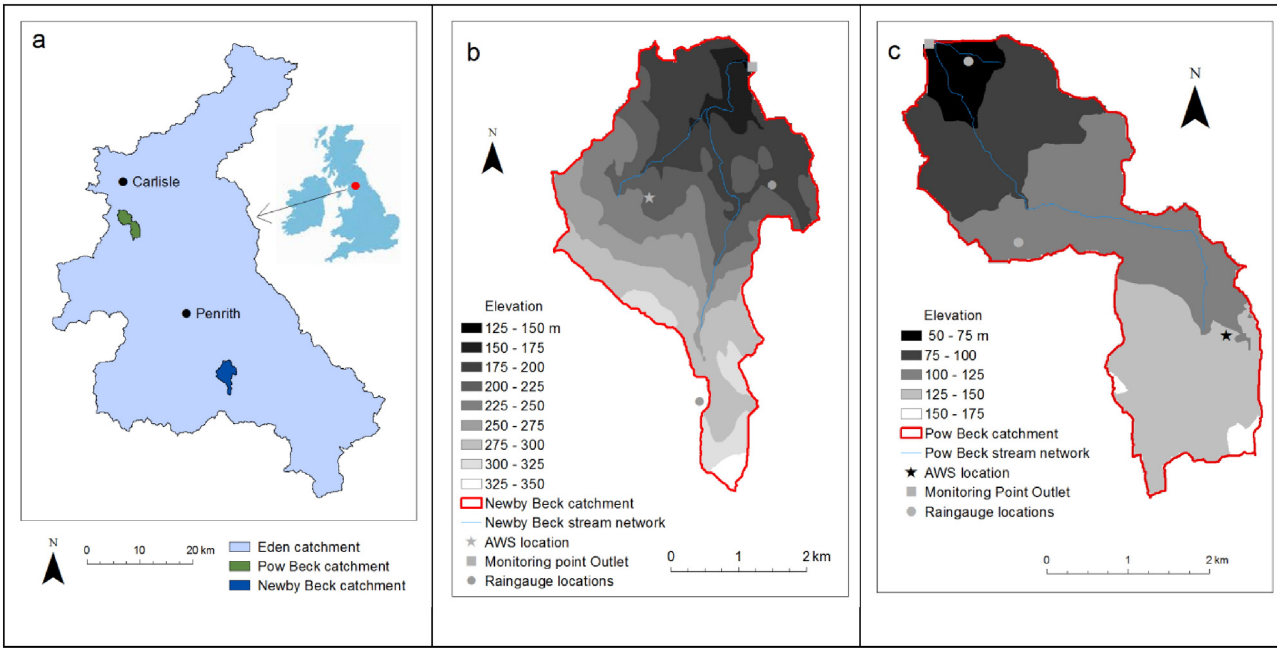

Fig. 1. Location (a) and topography of the Newby Beck (b) and the Pow Beck (c) catchments within the River Eden catchment, showing the monitoring stations. AWS = Automatic Weather Station. © OS Terrain 50 DTM [ASC geospatial data], Scale 1:50,000, Tiles: ny34, ny35, ny44, ny51, ny52, ny61, ny62, Updated: July 2013, Ordnance Survey (GB), Using: EDINA Digimap Ordnance Survey Service, <http://digimap.edina.ac.uk>, Downloaded: Tue. May 13 09:17:28 BST 2014.

defined as Principal Aquifers (Allen et al., 1997). Newby Beck lies on the Carboniferous limestone/mudstone layers, which are inclined towards the north-east and dip under the sandstone in the valley bottom. A cross-section of the Newby Beck catchment from the south-west to north-east is given in the Supplementary Information, showing the inclined layers. The inter-layering of shales/mudstones with more resistant limestone beds has resulted in a crenulated topography of scarp and dip slopes. Superficial deposits are extensive but shallow. A preliminary review of the geology and hydrogeology (Allen et al., 2010) indicates that aquifers may exist in the more permeable bedrock layers but that, because of the inclination of the layers, these are likely to be localised across the catchment. The degree of hydraulic interconnection between the bedrock and the river is unknown, but is currently under further investigation with establishment of a borehole programme.

Pow Beck is located in an interfluve position between the more deeply incised River Caldew to the west and the River Petteril to the east. The catchment lies primarily on the sandstone (Fig. 2), with a low relief cover of surficial deposits, up to 25 m in depth. Hydrogeological data from boreholes in the Pow catchment (Allen et al., 2010) indicate that groundwater levels are uniformly below the level of the river bed and thus that Pow Beck does not appear to gain water from the underlying aquifers at any point along its length. Water that passes through the superficial deposits and reaches the underlying aquifers leaves the catchment and does not contribute to the flow in Pow Beck. Thus, discharge in Pow Beck is a combination of surface runoff and discharge through the superficial deposits.

Land use in both catchments is primarily improved grassland, used for dairy, beef and sheep, with small areas of arable (6% in Newby Beck, 37% in Pow Beck). This is typical of large catchment areas of north-west England. Soils are generally slowly permeable, seasonally waterlogged loams, with well-drained loamy soils in the higher areas of the Newby Beck catchment. The characteristics of these two catchments are summarised in Table 1, including current WFD status.

2.2. Future rainfall projections

Future rainfall projections for Pow Beck and Newby Beck were determined from the UK Climate Projections Weather Generator (UKCP, 2009). The UKCP09 Weather Generator provides plausible multiple daily and hourly time series of weather variables, which are statistically equivalent and stationary (Jones et al., 2010). For each run, these are:

- For one location or area
- For a 30-year baseline period and one 30-year scenario period (e.g. 2050s, which covers 2040–2069)
- For one UKCP09 emission scenario.

In this study, rainfall for each catchment was determined from the UKCP 5 km × 5 km grid boxes (i.e. cell size 25 km^2) which covered it (for Pow: 3400550; 3450550; for Newby: 3650525; 3600525; 3600520; 3650520). Rainfall in these 5 km × 5 km cells is downscaled by the Weather Generator from the climate model ensemble (25 km resolution) which underpins the UKCP09 probabilistic projections (Murphy et al., 2009). The downscaling is justified, as the 5 km grid captures the significant spatial signature which is in the long-term observational weather and climate data (Jones et al., 2010). The use of an ensemble of models within UKCP09 results in the probabilistic projections and ensures that the rainfall projections for a single representative grid cell are more robust (Kendon et al., 2008). For each catchment, 100 runs of 30 years (3000 years in total) were downloaded for baseline conditions (trained on long term observations 1961–1995) and for the 2050s, medium emissions scenario. Annual, winter (defined as December, January and February) and summer (defined as June, July and August) median averages and percentiles for rainfall were calculated. For Newby Beck, for each 30 year time series of hourly data, rainfall events with rainfall total greater than 10 mm were identified, by summing the hourly rainfall in periods separated by at least 6 h with no rain. The events thus identified were classified into bands: 10–20 mm; 20–30 mm etc. and the frequency of events in each band was calculated. The median frequency in each band and the 5th and 95th percentiles for frequency in each band were calculated from the histograms for each of the 100 runs.

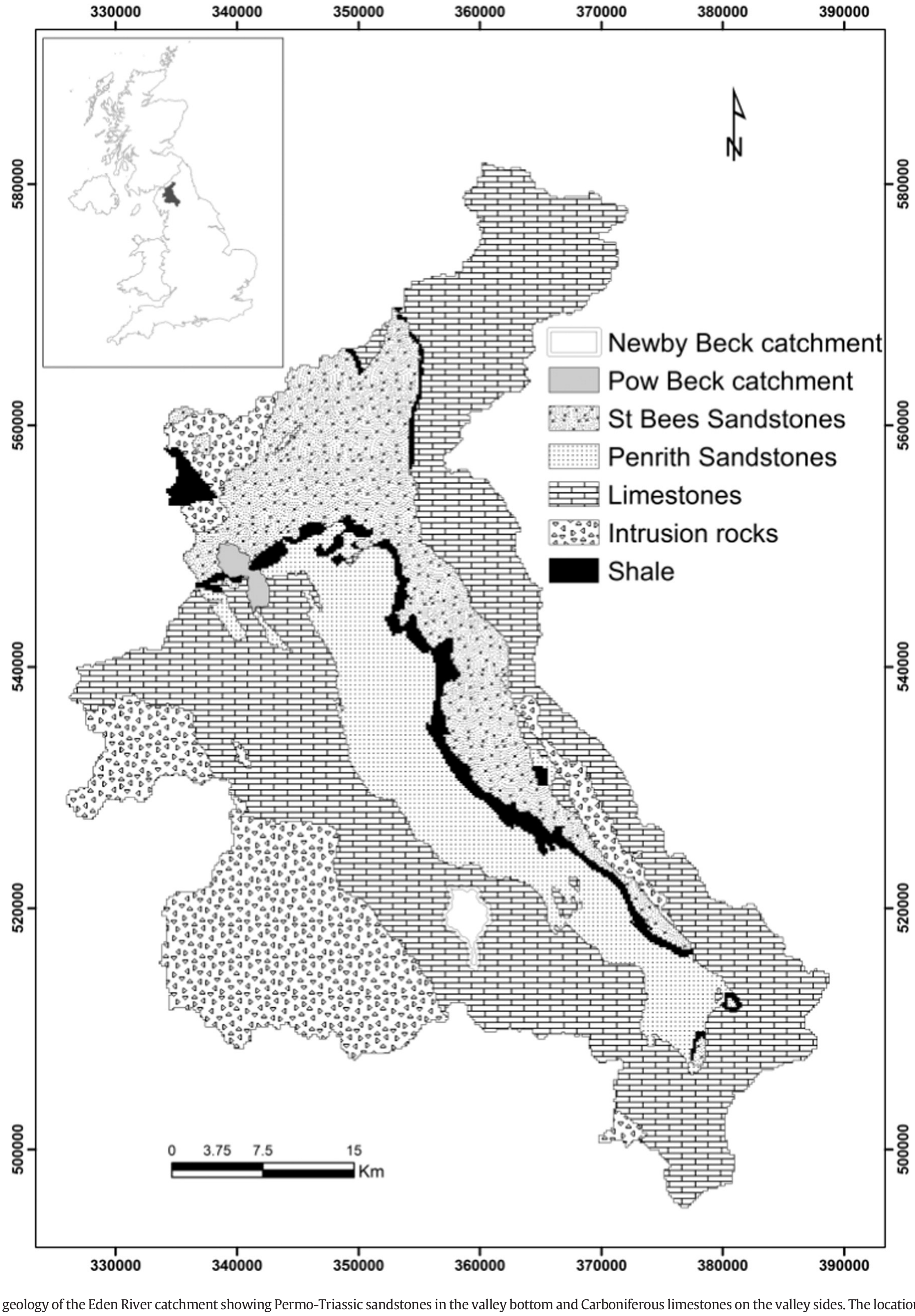

Fig. 2. Bedrock geology of the Eden River catchment showing Permo-Triassic sandstones in the valley bottom and Carboniferous limestones on the valley sides. The locations of the Newby Beck and Pow Beck catchments are shown. *Reproduced with the permission of the British Geological Survey ©NERC. All rights Reserved.*

2.3. High frequency river data

All data were collected by EdenDTC as part of the national DTC programme. Data for Newby Beck covered the period 1 October 2011–30 September 2012; data for Pow Beck covered the period 1 April 2012–31 March 2013. In each case, the period covered the 12 consecutive months with least missing data. Consequently, the data from these periods is not directly comparable. They are not presented as a

Table 1
Summary characteristics of the Newby Beck and Pow Beck catchments.

Monitored location		Newby Beck at NY 600 213 54.59°N, 2.62°W	Pow Beck at NY 386 501 54.84°N, 2.96°W
Monitored elevation (m A.S.L)		151	60
Area (km^2)		12.5	10.5
Average rainfall (mm)[a]		1203 ($\sigma = 167$)	882 ($\sigma = 112$)
Base Flow Index (BFI)		0.39	0.38
Average slope (°)		4°	1°
Geology		Glacial till over fractured Carboniferous limestone/mudstone	Glacial till over sandstone
Soil association[b]		711n Clifton (20%) 713 g Brickfield 3 (60%) (slowly permeable, seasonally wet, fine loamy) 541 q Waltham (20%) (well drained, fine loamy)	711n Clifton (100%) (slowly permeable, seasonally waterlogged, fine and coarse loamy)
WFD status[c]	Overall	Poor[d] (due to fish)	Poor[e] (due to phosphates and fish)
	Phosphates	High[d]	Poor[e]
Land Use (%)[f]	Arable	6	37
	Improved pasture	76	46
	Rough grazing	14	12
	Woodland	2	6
	Urban	0.7	0.4

[a] Based on Met Office long term average data for 5 km grid, 1981–2000 (Met Office, 2009).
[b] From Soil Survey of England and Wales (1983).
[c] WFD status from 2014 Cycle 2.
[d] Water body sampled on Morland Beck at NY601220, approx. 1 km downstream of Newby Beck outlet.
[e] Water body sampled on Pow Beck at NY397481, approx. 3 km upstream of Pow Beck outlet.
[f] Based on CEH Land Cover Map LCM2007 (CEH, 2007).

comparison but rather as two separate datasets which illustrate high frequency dynamics, from which it is possible to learn about the catchments and the hydrological and biogeochemical processes.

In each catchment, precipitation was measured at an Environmental Measurement Limited (EML) automatic weather station, plus two further Casella 0.2 mm tipping bucket rain gauges (Fig. 1). These were combined by area weighting to give a time series at 15-min resolution. Discharge or flow (Q) at each catchment outlet was estimated from stage data logged at 15-min intervals by a barometric diver (Schlumberger, Portland, OR, USA), converted to discharge data using application of a rating curve based on gauged flows ($n = 14$ for Newby Beck; $n = 9$ for Pow Beck).

Turbidity was determined at 15-min intervals with a YSI sonde (Sontek/YSI Inc., San Diego, USA) mounted in a flow-through reservoir at the sampling station at each catchment outlet. Suspended sediment (SS) was measured by collection and analysis of water samples and used to build up a SS concentration-turbidity rating (Perks et al., 2015). This relationship was applied to turbidity data to approximate a sediment dataset, and allow comparison of N, P and SS loads.

Nutrient data (total phosphorus (TP), total reactive phosphorus (TRP), and nitrate (NO_3^-)), were determined in-situ with a Hach Lange combined Sigmatax sampling module and Phosphax analyser (Jordan et al., 2007; Jordan et al., 2013; Perks et al., 2015). A flow-through reservoir was refreshed at 30-min intervals, from which samples were drawn for TP and TRP analyses. The Sigmatax–Phosphax analyser measures TP and TRP alternately by acid digestion and colorimetry, with the digestion omitted on the TRP cycle. Each analysis takes approximately 10 min. Nitrate was determined with a Nitratax Plus SC optical probe. This resulted in a 30-min resolution data set for nutrients.

2.4. Data analysis

Analysis was undertaken on hourly data and at different timescales: event, monthly and annual; and considered at different flow types: high flow ($>Q_{10}$), mid flow (Q_{90}–Q_{10}) and low flow ($<Q_{90}$), where Q_{10} is the discharge exceeded 10% of the time (90th percentile) and Q_{90} is the discharge exceeded 90% of the time (10th percentile). Hourly data were considered to be of sufficient resolution at the study sites to represent the high frequency dynamics and contain the most information on catchment behaviour. Where data were collected at higher frequencies, the data were summed (rainfall) or averaged (discharge, nutrients) over each hour.

Events were classified according to the relative dynamics of TP concentration (C_P) and discharge (Q), following the method of Haygarth et al. (2004), into Type 1 (high Q, low C_P), Type 2 (high Q, high C_P) or Type 3 (low Q, high C_P) (Fig. 3). Events were identified by times when either the discharge or the TP concentration exceeded a threshold value, chosen to be Q_{10} and C_{P10} respectively. The start of the event was defined as the beginning of the rainfall period that resulted in an increase in discharge. Where rainfall was intermittent, the start of a new event had to be preceded by at least 6 h with no rain. The end of

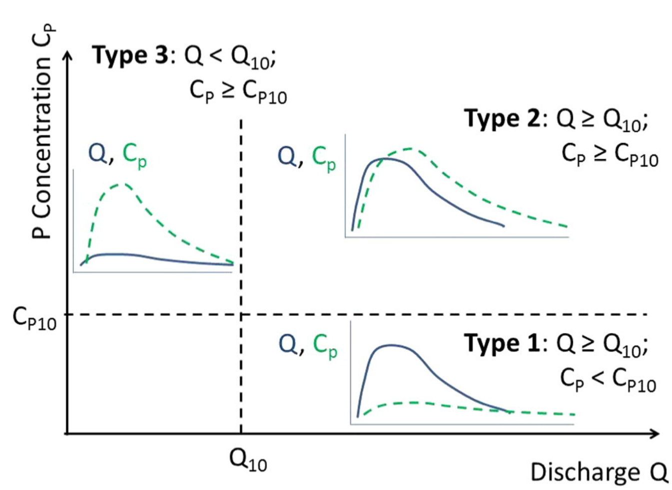

Fig. 3. Event classification method, according to the method of Haygarth et al. (2004) depending on the relative dynamics of the discharge (Q, blue solid line) and phosphorus concentration (CP, green dashed line). Q_{10} is the discharge exceeded 10% of the time; C_{P10} is the concentration of total phosphorus exceeded 10% of the time. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the event was defined as the time when both discharge and concentrations returned to below the threshold level.

The annual transported loads of sediment and nutrients were calculated using:

$$Load_j = K_j \sum_{i=1}^{n} Q_i C_{ij} \Delta_t \quad (1)$$

where $Load_j$ is the total annual flux of determinand j, K_j (=100/percentage of data) is a correction factor to scale the annual load according to the percentage of data which is missing, Q_i is the discharge at time i, C_{ij} is the concentration of determinand j at time i, Δt is the length of each timestep and the summation is over all time steps in the year of data. Event loads were calculated by the same method, with the sum taken over the period that Q_{10} was exceeded.

The sensitivity of TP transfers to rainfall events in the future, (i.e. assuming no changes in agricultural practices or changes in hydrological or biogeochemical processes), were estimated using a simple linear regression between event rainfall and event TP load, combined with the frequency of events in each category, i.e.

$$Annual\ Event\ TP\ load = \sum_i Event\ TP\ load_i . Frequency_i \quad (2)$$

where $Event\ TP\ load_i$ is the load for an event in rainfall category i, calculated from the linear regression using the central value of the rainfall category and $Frequency_i$ is the frequency of events in rainfall category i, calculated from the UKCP Weather Generator data. Rainfall categories were 10–20 mm, 20–30 mm, etc.

Seasonal contributions were assessed by constructing concentration duration curves for TRP and nitrate for each calendar season, in order to compare observed concentration dynamics with WFD target levels. Site specific reactive phosphorus (RP) targets for WFD standards in England and Wales were calculated according to UK TAG guidelines (WFD-UKTAG, 2014), using catchment altitude and alkalinity. Total RP data are directly comparable with RP from Environment Agency routine monitoring, which is also determined on an unfiltered sample.

3. Results and discussion

3.1. Observed rainfall and projected rainfall changes

The observed rainfall for the 12 months reported in this study was 1205 mm for Newby Beck (1 October 2011–30 September 2012) and 1041 mm for Pow Beck (1 April 2012–30 March 2013). The differing periods of observation are not important, as the catchments are not being compared to each other, but to the long term averages (for each catchment separately) and the probabilistic distributions from UKCP09 Weather Generator. Compared to the longer-term averages (Table 1), the observations were close to average for Newby Beck (the year included a dry winter and a very wet summer) and high for Pow Beck (the monitored year included the very wet summer and autumn of 2012, but not the preceding dry winter), but still well within two standard deviations of the mean which covers the inter-annual variability 95% of the time. The projected annual and seasonal rainfall in the Pow Beck and Newby Beck catchments are given in Table 2. The longer term averages from Table 1 lie within the upper half of the distributions of baseline values in Table 2, but the UKCP09 baseline projections are trained on observed rainfall 1961–1995, compared to 1981–2000 for the averages in Table 1. The total annual rainfall is projected to increase slightly in each catchment (% change in median and percentiles are all positive, with 3% change in median for Pow Beck), but the changes in the seasonal rainfall are much more marked. Winter rainfall for Pow Beck is projected to increase by 8–17% (10th–90th percentiles), and summer rainfall to decrease by 9–26%, with similar changes projected for Newby Beck. Although total summer rainfall is projected to decrease, it is likely that future rainfall will be concentrated into fewer, more intense summer storms as identified for the south of the UK by Kendon et al. (2014).

Event rainfall analysis on the UKCP09 data for Newby Beck indicated that events larger than 10 mm were projected to increase in number and to make up a larger percentage of the annual rainfall between the baseline conditions and the 2050s (Table 3). The rainfall total in the largest events (95th percentile, 99th percentile and maximum over 100 runs) indicated a shift in the distribution towards larger events. When the events were categorised into bins (10–20 mm, 20–30 mm etc.), the median frequency of events in each rainfall category was larger for the 2050s than for the baseline conditions (Fig. 4). The median frequency was significantly different at the 99% confidence level (Kruskal–Wallis non-parametric test, $p < 0.01$) for all rainfall categories except 10–20 mm.

3.2. Overall response

Flow in both catchments was characterised by frequent discharge events occurring in response to regular rainfall inputs. Hydrographs were flashy, rising steeply with minor attenuation of falling limbs during individual storm events. Fig. 5 shows the dataset for Newby Beck, illustrating that peaks in SS and TP/TRP occurred frequently and

Table 2
Projected annual, winter and summer rainfall in mm (median, 10th and 90th percentiles) for Pow Beck and Newby Beck catchments, from UK Climate Projections (UKCP09[a]), for baseline conditions and under 2050s medium emissions scenario, with % change.

Pow Beck	Baseline			2050s			% change		
Percentile	10th	50th Median	90th	10th	50th Median	90th	10th	50th Median	90th
Annual rainfall	708	828	954	713	849	994	+1%	+3%	+4%
Winter rainfall DJF	154	215	283	174	246	332	+8%	+14%	+17%
Summer rainfall JJA	147	201	262	109	167	238	−26%	−17%	−9%

Newby Beck	Baseline			2050s			% change		
Percentile	10th	50th Median	90th	10th	50th Median	90th	10th	50th Median	90th
Annual rainfall	884	1054	1231	885	1073	1290	+0%	+2%	+5%
Winter rainfall DJF	232	329	443	251	362	503	+8%	+10%	+14%
Summer rainfall JJA	145	198	262	107	165	239	−26%	−17%	−9%

[a] UKCP, 2009. The UK Climate Projections (UKCP09) have been made available by the Department for Environment, Food and Rural Affairs (Defra) and the Department of Energy and Climate Change (DECC) under licence from the Met Office, UKCIP, British Atmospheric Data Centre, Newcastle University, University of East Anglia, Environment Agency, Tyndall Centre and Proudman Oceanographic Laboratory. These organisations give no warranties, express or implied, as to the accuracy of the UKCP09 and do not accept any liability for loss or damage, which may arise from reliance upon the UKCP09 and any use of the UKCP09 is undertaken entirely at the users risk.

Table 3
Event rainfall analysis on UK Climate Projections data (UKCP, 2009) for Newby Beck. Events had a rainfall total > 10 mm, with the start and end of the event identified by at least 6 h with no rain.

Newby Beck	Baseline	2050s
No. of events > 10 mm (for 30 year run, mean over 100 runs)	944	986
Percentage of total rainfall in events >10 mm	62%	67%
Event rainfall 95th percentile (mean over 100 runs)	46	50
Event rainfall 99th percentile (mean over 100 runs)	70	79
Maximum event rainfall (mean over 100 runs)	119	140

rapidly in response to rainfall, with TP concentrations often exceeding 0.6 mg L^{-1}. More than 60% of TP transported through the Newby Beck catchment outlet was particulate in both winter and summer, with lower concentrations in the TRP fraction, which represented 38% of TP transfer on average over the monitoring period.

The site-specific WFD target levels for RP in Newby Beck are shown in Fig. 5. On average, TRP in Newby Beck was 0.041 mg L^{-1}, which would be classified as 'good', although this deteriorated to 'moderate' or 'poor' during storms. Phytobenthos (an ecological indicator under WFD) demonstrates that these periods of lower phosphorus standards are associated with lower ecological status (Snell et al., 2014). Under the WFD, there are no accepted targets for turbidity or suspended sediment in rivers, although the need for targets which consider the relationship between sediment pressures and ecological condition (Wood and Armitage, 1997) has been identified (Bilotta and Brazier, 2008; Collins et al., 2011). The annual mean SS concentration was 9.5 mg L^{-1}, with a concentration of 25 mg L^{-1} exceeded for 6% of the year, during storm events. Nitrate concentrations in drinking water are restricted to 50 mg L^{-1} (11.3 mg N L^{-1}), and these targets were not exceeded for Newby Beck for the year shown (Fig. 5).

The data from Pow Beck showed similar characteristics (Fig. 6). For the year in this study, the annual mean SS concentration was 16.2 mg L^{-1}, with a SS concentration of 25 mg L^{-1} exceeded for 16% of the year. TP and TRP concentrations were generally higher than for Newby Beck, with an average TRP concentration of 0.20 mg L^{-1}. TRP represented 62% of TP transfer. The nitrate limit was not exceeded in Pow Beck for the year shown.

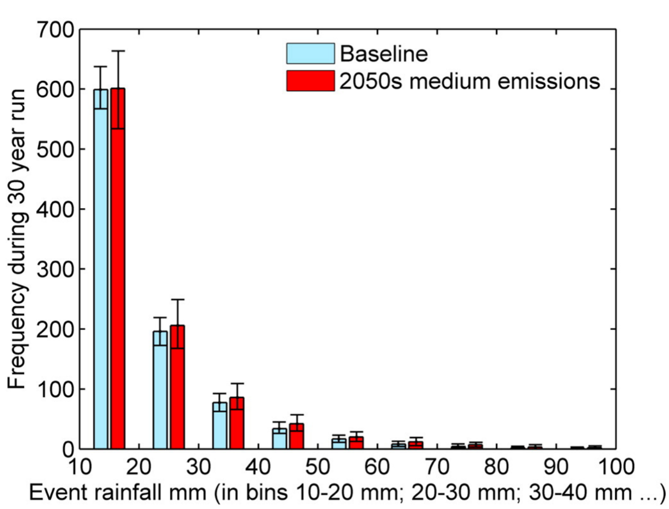

Fig. 4. Projected frequency of rainfall events in Newby Beck derived from UK Climate Projections Weather Generator (UKCP, 2009), grouped in 10 mm bins for events 10 to 100 mm, for baseline conditions and 2050s. Bars indicate the median frequency, whiskers indicate the 5th and 95th percentiles of frequency over 100 runs. Events larger than 100 mm have been excluded from the graph but represent less than 1% of events.

3.3. Event classification

Event classification (Table 4) shows that in both catchments more than 80% of the TP load was transferred through the monitored outlet in high flow events (Type 1 and 2), supporting findings from monitoring in other agricultural headwater catchments (e.g. Jordan et al., 2007). Although there were several Type 3 events in each catchment (11 in Newby Beck, 28 in Pow Beck), these tended to be short in duration and because discharge was not high, the load transferred during these events was negligible. Some of these Type 3 events were when only small discharge responses (<Q10) to rainfall occurred following dry periods. Others occurred with no discharge response at all, but both P and nitrate concentrations peaked together, suggesting a point source rather than event-driven input from diffuse sources that are activated and linked to streams during rainfall and runoff. These were more numerous in Pow Beck (up to 7 events) than in Newby Beck. Although loads during Type 3 events were low, high concentrations (e.g. SS and P) during these low flow periods can have an adverse ecological impact (Bilotta and Brazier, 2008; Chetelat et al., 1999).

Figs. 7 and 8 show typical event responses for the Newby Beck catchment. All event responses are summarised in tabular form in the Supplementary Material. There was a seasonal change in the pattern of nitrate responses throughout the year. In autumn/winter, nitrate concentrations were initially reduced by rainfall events, reflecting dilution in the river, followed by a delayed damped peak 6–13 h after peak flow and then gradually falling to base flow levels (Fig. 7), whereas SS, TP and TRP all showed relatively sharp peaks in concentration correlated with increased flow. In contrast, during spring and summer storms, nitrate concentrations increased more rapidly in response to rainfall and increased flow (0–7 h after peak flow) with peaks of greater magnitude (Fig. 8).

These data demonstrate that, for both these catchments, rainfall was the dominant driver of the diffuse sediment and P response. Activated rainfall-driven sources (e.g. rain splash erosion of bare surface soils, mobilisation of instream sources including exposed channel banks and deposited bed sediment, flushing through field drains) delivered sediment and nutrients to the stream network via relatively fast pathways. The sediment and TP responses were almost concurrent with discharge (highest cross correlation with discharge at time lag of 0 h), and approximately three hours behind peak rainfall, indicating fast pathways such as surface runoff or tile drains, both of which have been observed in the catchments. Chappell et al. (2007) suggest that information about the dominant flow pathways can be deduced from knowledge on the presence or absence of four types of strata (topsoil, subsoil, permeable regolith, permeable rock). For example, a thin layer of topsoil over impermeable rock would result in a very fast response time in the hydrograph (time constant of minutes to hours), whereas the water movement through all four layers would show as a very damped and slow response in the hydrograph (time constant of weeks to months). Groundwater can be an important pathway for nutrient transport in some catchments, particularly for nitrate but also sometimes for P (Holman et al., 2010). This highlights the importance of hydrogeological research at a study site. For both of the catchments in this study, the flashiness of the hydrological response and the short time lag between the discharge and TP response is consistent with fast pathways such as surface runoff or flow through tile drains. TRP (highest cross correlation with discharge at time lag of only 2 h), also suggested fast pathways, though because of the delay and damped nature of the response, these were more likely to be fast sub-surface flow pathways, such as flow through the topsoil or subsoil. In the future, with the projected increase in winter rain (Table 2) and the increased likelihood of more intense rainfall in both winter and summer, rain splash erosion (due to rainfall kinetic energy) and mobilisation of instream sources (flashier discharge will mobilise bed sediment and scour exposed channel banks) will become even more important. If all other contributing factors (such as land use, soil cover, land

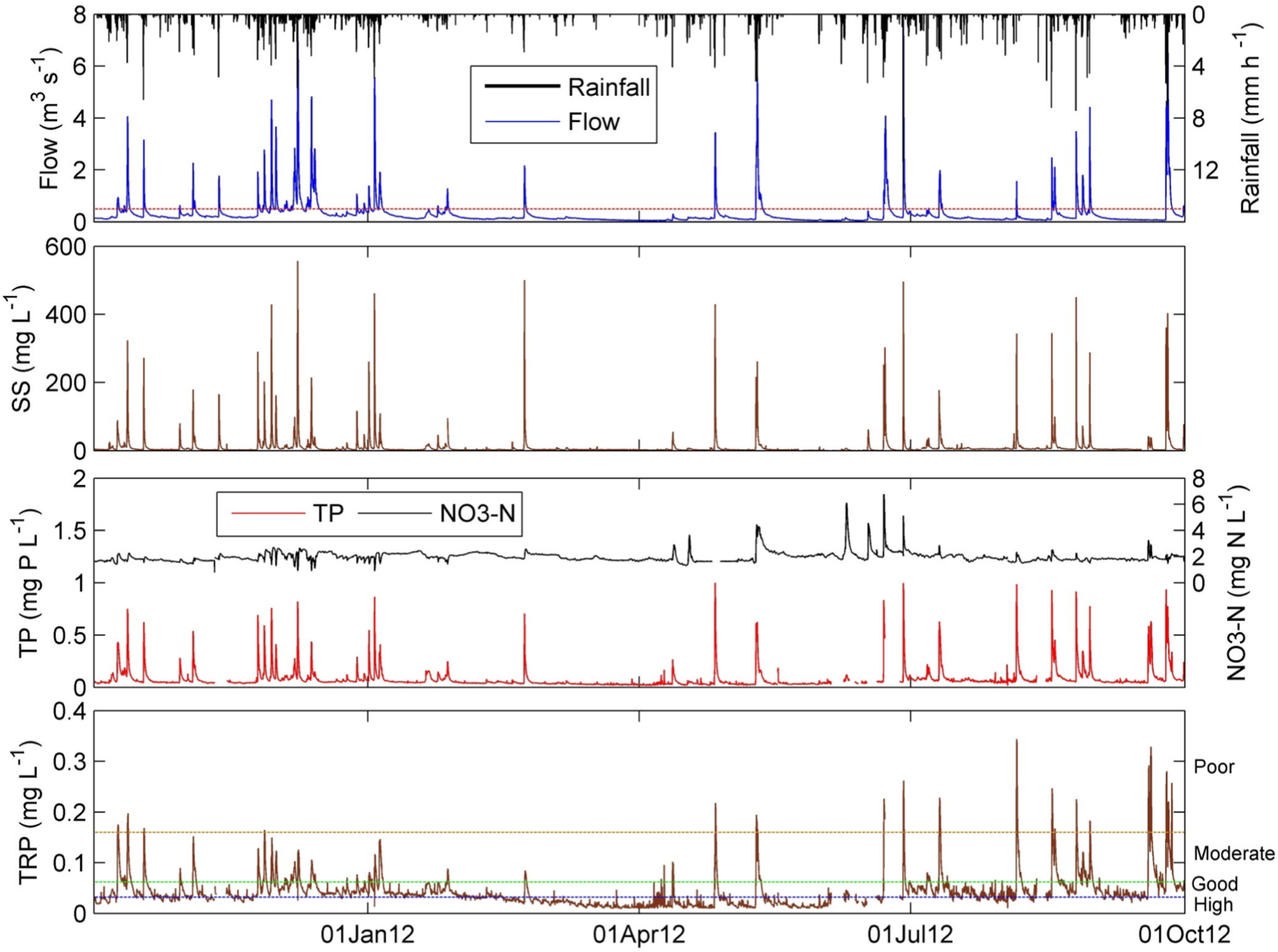

Fig. 5. Rainfall, flow and water quality data for 1 October 2011–30 September 2012 for the Newby Beck catchment. Suspended sediment (SS) data are calculated from 15 min resolution turbidity measurements, using a SS concentration–turbidity rating. Data for total phosphorus (TP), total reactive phosphorus (TRP) and nitrate-N (NO_3–N) are high resolution, half-hourly data from on-site analysis. The horizontal line on flow is Q_{10}, the discharge exceeded 10% of the time. The horizontal lines on TRP represent the current WFD upper boundaries for reactive P to achieving the water quality standards, calculated using UK TAG guidelines (WFD-UKTAG, 2014).

management practices) remained the same, and assuming no limit to P supply in the longer term, this would lead to more pollution in surface waters and a deterioration in ecological status. As future changes in land use and land management practices are unknown, and are determined more by economics, policy and legislation (also as yet unknown) than by climate change, these results illustrate how the projected rainfall changes would affect the 'business as usual' scenario. The results therefore present an opportunity for farmers and land managers (ideally supported by policy) to manage some of the other contributing factors in a way which might offset the effects of a variable climate. For example, good soil nutrient status and nutrient source management could be rewarded to ensure that soils are not over-fertilised or that applications of manure are not made at inappropriate times. For livestock farmers in high rainfall areas, building larger, covered slurry stores (preferably with policy support to help overcome the social and economic challenges faced by farmers) would enable them to store slurry for longer and avoid the necessity to spread when stores are full. Other measures such as cover crops (which can help to reduce mobilisation of sediment and nutrients) or retention ponds (which can help to reduce delivery of sediment and nutrients to streams) could be supported through voluntary environmental schemes with financial incentives (e.g. McDowell et al., in press).

For nitrate, the seasonal change in response indicated a change in sources, with dilution (Fig. 7) indicating a fast pathway which carried relatively little nitrate. Events with a nitrate peak that responded rapidly to rainfall (e.g. Fig. 8) suggest a fast pathway connected to an additional nitrate source such as recently applied fertiliser. The nitrate peak that followed dilution or extended the response suggested a slower sub-surface pathway connected to an old nitrate source such as displacement of nitrate in sub-surface pore water. However, the response time of this pathway is still relatively fast (hours rather than days), thus, according to Chappell et al. (2007), again suggesting a shallow pathway. Nitrate levels are known to be high, and rising, in the sandstone aquifer in the bottom of the Eden Valley (Butcher et al., 2006) and whilst the hydrogeology of the catchments (Allen et al., 2010) suggests that the deep groundwater does not contribute to the outflow of these study catchments, it is possible that some nitrate leaves the catchments through the soil and rock and may eventually contribute to the nitrate in the sandstone aquifer, which may subsequently return to the surface further down the larger Eden catchment. It is important to consider all the sources contributing to diffuse nutrient pollution; for similar studies in other catchments, different sources may have more relative importance. Information on the geology and hydrogeology is particularly important in catchments dominated by groundwater input, and should be included as part of the research. Similarly, the contribution from atmospheric deposition of inorganic nitrogen is important in some catchments, particularly if only a small part of the catchment is dominated by agriculture, or if air pollution from anthropogenic emissions is bad. An assessment of the relative contributions of different sources (e.g. Gao et al., 2014) is a useful way to assess which are most

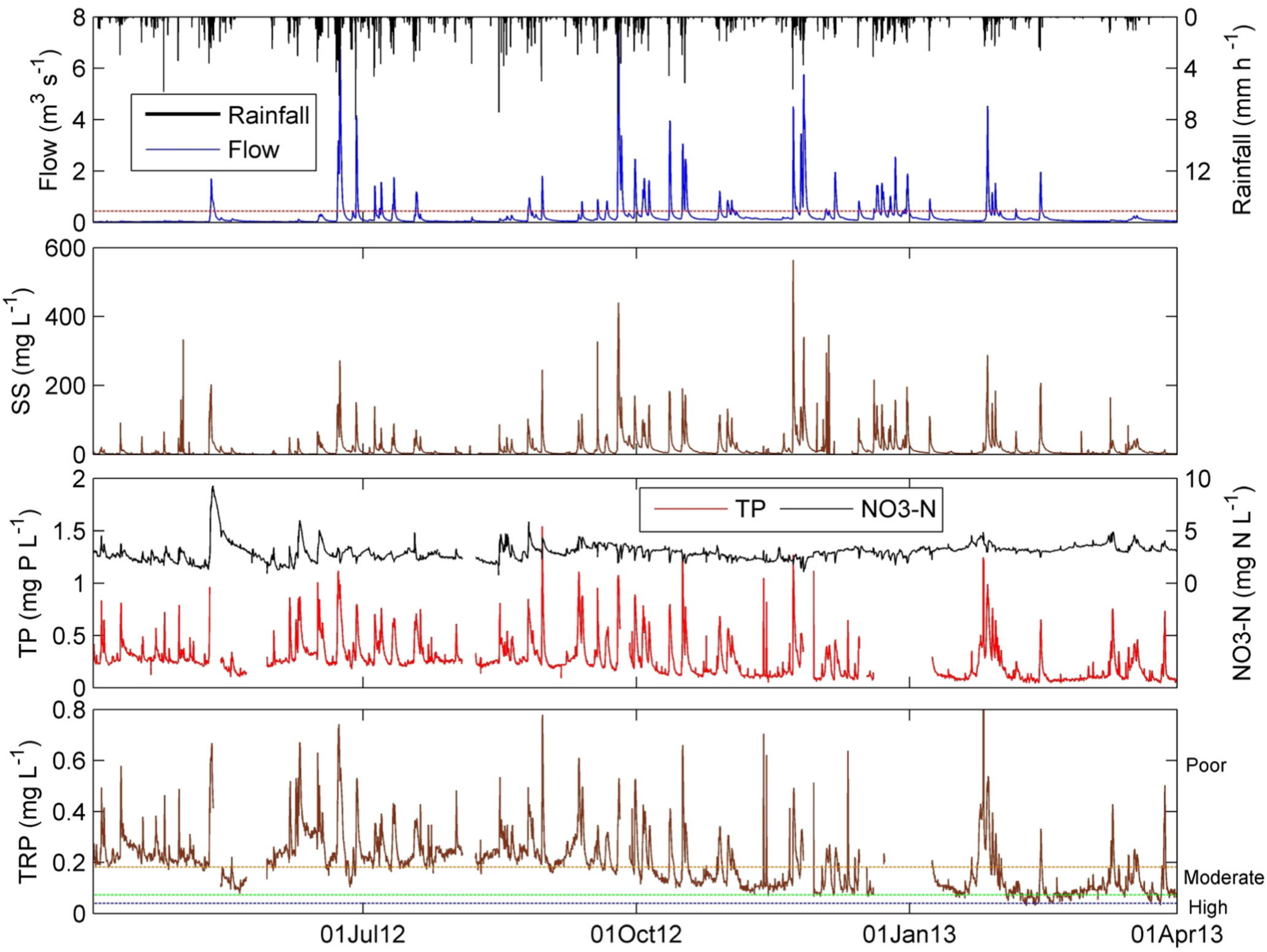

Fig. 6. Rainfall, flow and water quality data for 1 April 2012–30 March 2013 for the Pow Beck catchment. Suspended sediment (SS) data are calculated from 15 min resolution turbidity measurements, using a SS concentration–turbidity rating. Data for total phosphorus (TP), total reactive phosphorus (TRP) and nitrate-N (NO_3–N) are high resolution, half-hourly data from on-site analysis. The horizontal line on flow is Q_{10}, the discharge exceeded 10% of the time. The horizontal lines on TRP represent the current WFD upper boundaries for reactive P to achieve the water quality standards, calculated using UK TAG guidelines (WFD-UKTAG, 2014).

important. For the agriculturally-dominated catchments in this study, in a region with very little air pollution, inputs of inorganic nitrogen from the atmosphere were considered negligible in comparison with fertiliser and manure inputs.

In both Pow Beck and Newby Beck, the highest event rainfall total did not result in the highest TP concentration (see Supplementary Material). This could be due to the sustained nature of the rainfall rather than the maximum intensity, or to flushing of P during smaller events in previous days, or because the event with highest rainfall did not happen to follow immediately after a fertiliser or slurry application. However, total event rainfall was a good predictor of event TP load (Fig. 9), suggesting that if average event rainfall increases in future (as in Fig. 4), with the occurrence of a greater number of extreme events, then P loadings to rivers could also increase. There were a few exceptions to this pattern (Fig. 9a), which could be attributed to antecedent conditions (Fig. 9c). In this example from Pow Beck, an event following a dry period resulted in little flow response to the rainfall, but a high TP concentration (Type 3 event). Withers and Hodgkinson (2009) also recorded high soluble reactive P and TP in low flow volumes entering an agriculturally dominated headwater stream during dry summer conditions. Higher P concentrations released to soil solution following drying and rewetting have been observed in laboratory experiments (Blackwell et al., 2009; Turner and Haygarth, 2001) and the same phenomenon may be what is observed here, similar to the flush of P observed after rewetting of soils after a dry summer (Dupas et al., 2015). Other outliers, with lower than expected event TP load for any given event rainfall could be attributed to exhaustion flushing of P when several events followed in quick succession (i.e. supply-limited rather than transport limited). However, as observed in (Fig. 9), this effect is small, otherwise the non-linearity would be indicated by much more scatter.

The event analysis in this study illustrates two issues of concern related to climate change: firstly, the predicted increase in winter rainfall (Table 2) and the increase in number of extreme events is likely to

Table 4
Event classification for the Newby Beck and Pow Beck outlets for one year each, showing the importance of high discharge events for total phosphorus (TP) transfer.

Newby Beck 1 Oct. 2011–30 Sept. 2012	$Q_{10} = 0.49\ m^3\ s^{-1}$ $C_{P10} = 0.13\ mg\ L^{-1}$	No. of events	% of TP load
Type 1	$Q \geq Q_{10}$; $C_P < C_{P10}$	1	1%
Type 2	$Q \geq Q_{10}$; $C_P \geq C_{P10}$	31	83%
Type 3	$Q < Q_{10}$; $C_P \geq C_{P10}$	11	1%
Total		43	85%

Pow Beck 1 Apr. 2012–31 Mar. 2013	$Q_{10} = 0.44\ m^3\ s^{-1}$ $C_{P10} = 0.46\ mg\ L^{-1}$	No. of events	% of TP load
Type 1	$Q \geq Q_{10}$; $C_P < C_{P10}$	4	0.3%
Type 2	$Q \geq Q_{10}$; $C_P \geq C_{P10}$	29	79%
Type 3	$Q < Q_{10}$; $C_P \geq C_{P10}$	28	2%
Total		61	81%

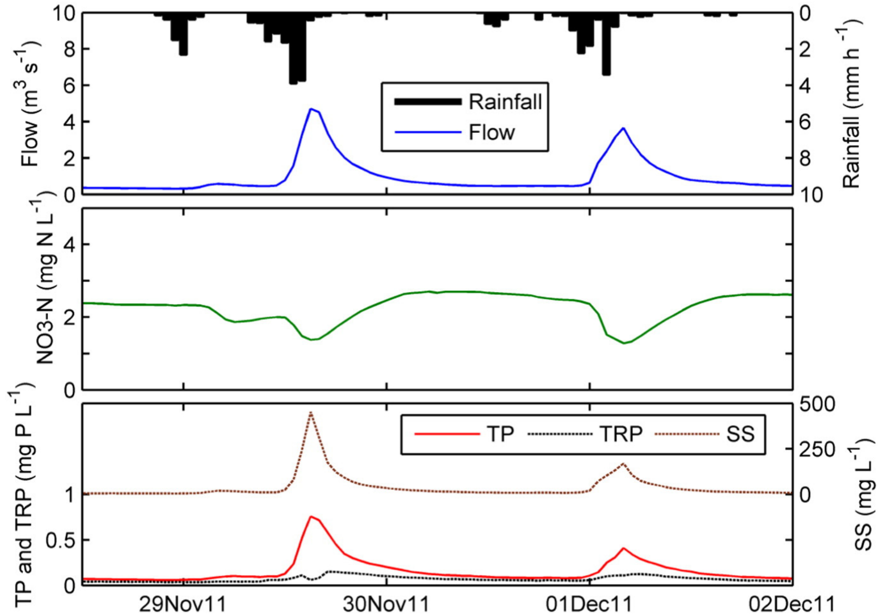

Fig. 7. Rainfall, flow, nitrate-N (NO_3–N), total phosphorus (TP), total reactive phosphorus (TRP) and suspended sediment (SS) at Newby Beck outlet for two Type 2 storms in November/December 2011, showing dilution of nitrate in winter storms, but high concentrations of SS and P correlated with flow peaks. Rainfall was 19.6 mm and 11.7 mm for the two storms, respectively.

increase the dominant rainfall-driven P transfers from land to water; secondly, the decrease in summer rainfall (Table 2) and the enhanced likelihood of extended periods of drying will result in longer periods of low flow, which will increase the in-stream concentrations of nutrients in rivers where groundwater dilution is not taking place. When this is followed by extreme rewetting it is also likely to enhance the concentrations of P reaching the waterways. The effect could be further enhanced by a global rise in temperatures. These two issues are consistent with the findings of Jordan et al. (2012).

The data from Newby Beck and Pow Beck cover different time periods (although both are 12 months in duration) and are not intended for comparison but as two separate examples of the high frequency dynamics observable in surface-water dominated systems. In spite of some big differences in catchment characteristics (topography, geology, land use), both catchments illustrate the same features in the high frequency dynamics, which further supports the messages relating to the potential effects of climate change on nutrient transfers.

3.4. Annual loads

Annual totals of rainfall, discharge and annual loads of SS, TP, TRP and Nitrate-N are given in Table 5 for both catchments, divided according to flow type.

High flows were particularly influential for SS and TP transfer, but less influential for nitrate transfers. Due to the time lag between peak flow and peak nitrate concentration (6–13 h), mid flows were also

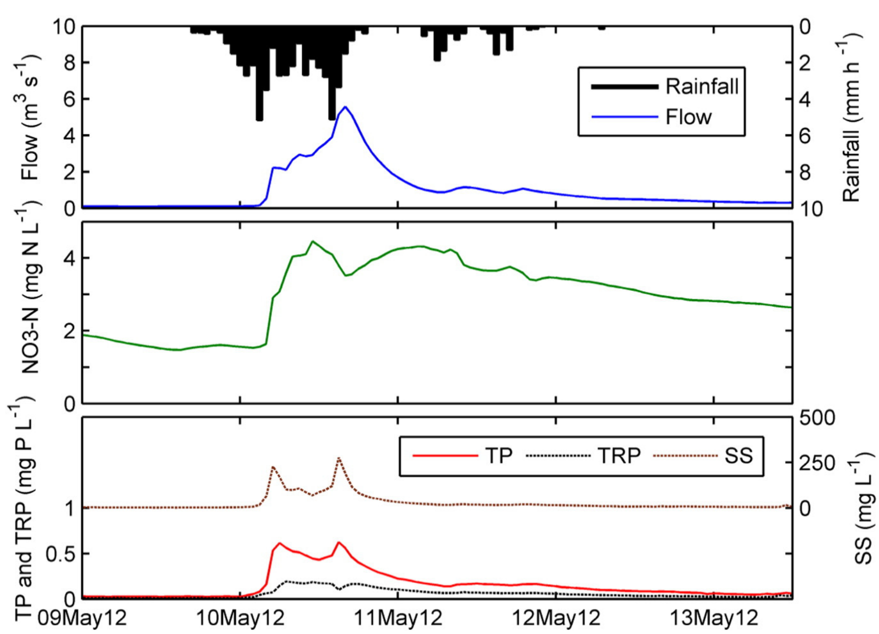

Fig. 8. Rainfall, flow, nitrate-N (NO_3–N), total phosphorus (TP), total reactive phosphorus (TRP) and suspended sediment (SS) at Newby Beck outlet for a Type 2 storm in May 2012, showing peaks in nitrate, SS, TP and TRP. Total event rainfall was 60.7 mm.

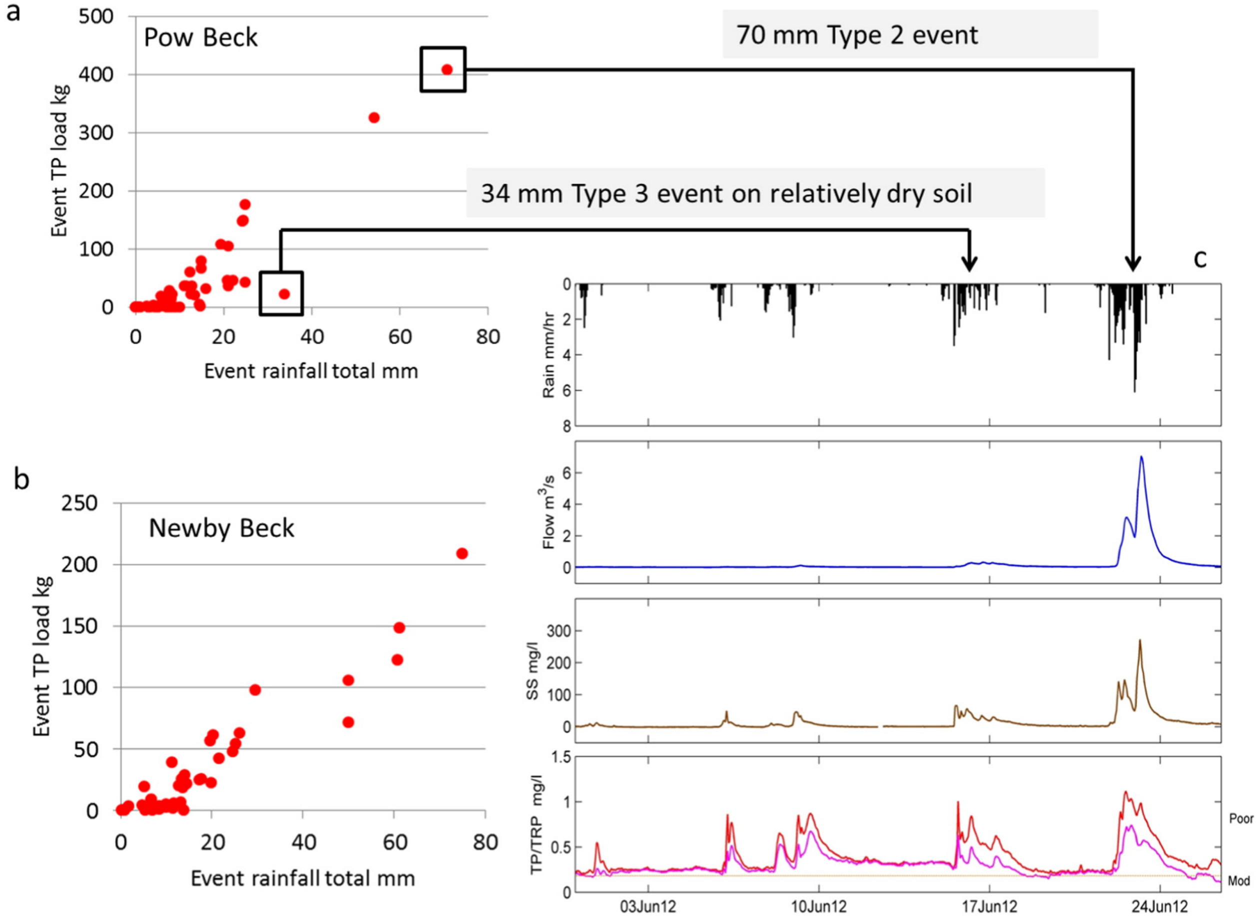

Fig. 9. Event rainfall total was a good predictor of the total phosphorus (TP) load at (a) Pow Beck ($R^2 = 0.81$) and (b) Newby Beck outlets ($R^2 = 0.90$). (c) The effect of dry periods in Pow Beck can explain some of the outliers. The relationship at Newby Beck: Event TP = (2.50 ± 0.27) Event Rain + (−11.56 ± 6.72) was used to model future TP transfers.

important for nitrate transfer through the catchment outlets (51% in mid flows at Newby Beck outlet, and 48% in mid flows at Pow Beck outlet). The proportion of the TP load as TRP was greater at low flow (67% at Newby Beck, 85% at Pow Beck) and mid flow (59% at Newby Beck, 73% at Pow Beck) than at high flow (32% at Newby Beck, 55% at Pow Beck). This suggests P release from sediments (Palmer-Felgate et al., 2009) or the presence of point source inputs, such as septic tanks, which contribute higher proportions of soluble P. Although the number of

Table 5
Annual loads for high flow, mid-low and low flow discharge for the Newby Beck and Pow Beck catchment outlets.

Newby Beck: 1 October 2011–30 September 2012; $Q_{10} = 0.492$ m^3 s^{-1}; $Q_{90} = 0.064$ m^3 s^{-1}.												
Total value	Rainfall		Q		SS		TP		TRP		Nitrate-N	
	mm	(%)	mm	(%)	tonnes	(%)	kg	(%)	kg	(%)	kg	(%)[b]
High flow (≥Q10)	423	35	326	46	410	93	1420	81	460	71	8680	48
Mid flow (Q90 ≤ Q < Q10)	724	60	369	52	30	7	320	18	190	29	9230	51
Low flow (<Q90)	58	5	13	2	0	0	10	1	0	0	320	2
Annual[a]	1205		708		440		1750		650		18230	
% data missing[b]	0		0		1.4		6.5		6.6		1.0	
Annual per ha					0.35		1.40		0.52		14.6	

Pow Beck: 1 April 2012–31 March 2013; $Q_{10} = 0.441$ m^3 s^{-1}; $Q_{90} = 0.027$ m^3 s^{-1}												
Total value	Rainfall		Q		SS		TP		TRP		Nitrate-N	
	mm	(%)	mm	(%)	tonnes	(%)	kg	(%)[b]	kg	(%)	kg	(%)
High flow (≥Q10)	314	30	392	56	530	91	3060	81	1700	76	10590	52
Mid flow (Q90 ≤ Q < Q10)	666	64	297	43	50	9	710	19	520	23	9720	47
Low flow (<Q90)	61	6	7	1	0	0	20	1	20	1	160	1
Annual[a]	1041		696		580		3790		2240		20470	
% data missing[b]	0		0		1.4		12.1		11.7		1.4	
Annual per ha					0.55		3.61		2.13		19.5	

[a] To estimate annual loads, calculated loads from high, mid and low flow bands have been scaled according to the percentage of data missing from each band, and rounded to the nearest ten tonnes or kg.
[b] Percentage loads may not total 100% due to rounding.

Table 6
Water Framework Directive (WFD) target values for Reactive Phosphorus (RP) for Newby Beck and Pow Beck and the percentage of year Total Reactive Phosphorus (TRP) falls within each WFD band. The RP target values have been calculated from the UK TAG guidelines (WFD-UKTAG, 2014). Contains UKTAG information © UKTAG and database right.

Newby Beck, altitude 151 m, alkalinity 250 mg L^{-1} $CaCO_3$; Mean TRP = 0.041 mg L^{-1}				
Target level	High	Good	Moderate	Poor
Reactive P (mg L^{-1})	<0.032	<0.062	<0.160	<0.971
Annual % time in RP target band	43	45	11	1
Pow Beck, altitude 60 m, alkalinity 175 mg L^{-1} $CaCO_3$; Mean TRP = 0.195 mg L^{-1}				
Target level	High	Good	Moderate	Poor
Reactive P (mg L^{-1})	<0.039	<0.073	<0.182	<1.024
Annual % time in RP target band	<1	4	41	54

septic tanks or small point sources in each catchment is unknown, as many are unregistered (Withers et al., 2013), the higher proportion of TRP in Pow Beck suggests that there are more (or better connected) small sources in that catchment.

3.5. Monitored responses in the context of WFD targets

The WFD targets for RP in the Newby Beck catchment are marked in Fig. 5. The average annual TRP concentration for hydrological year 2012 was 0.041 mg L^{-1}, which would have given Newby Beck overall 'good' WFD status for P (Table 6). This reflects the WFD ecological status, which was 'Moderate' over the same period, even though the range, based on monthly samples, spanned 'high' to 'poor' (Snell et al., 2014). The maximum TRP concentration recorded in Newby Beck was 0.379 mg L^{-1}.

The availability of high frequency concentration time series enabled construction of a concentration-duration curve for either annual data or for seasonal data. Fig. 10 indicates seasons of high concentration for TRP in Pow Beck and Newby Beck. This demonstrates when the WFD environmental standards for P were met and periods of highest risk for aquatic ecology. Fig. 10a indicates that in Pow Beck in summer, concentrations of TRP were 'poor' for almost the entire season, whereas in winter, concentrations of TRP were 'poor' for around 20% of the time and 'moderate' for most of the rest of the season. In contrast, TRP concentrations in Newby Beck (Fig. 10b) were 'poor' for only around 5% of the summer, and were 'good' or better for around 80% of the season.

Nitrate concentrations did not exceed target levels in either catchment, but the highest concentrations were recorded in late spring/early summer, coinciding with the fertiliser application period. Both the climate change effects which were highlighted earlier (the increased likelihood of extreme rainfall events and the increased concentrations during low flows) will affect the risk of WFD failure. In summer, or in periods of lower flow than during present day conditions, nutrients will become more concentrated; this will be particularly noticeable in catchments such as Pow Beck, which has a high background concentration of TRP, probably due to numerous small point sources, such as septic tanks. The presence of small point sources such as (possibly unregistered) septic tanks in rural catchments, which contribute to P pollution, is well recognised (Arnscheidt et al., 2007; Jordan et al., 2005b; May et al., 2012; Withers et al., 2011; Withers et al., 2013), but is often overlooked in planning diffuse pollution mitigation. Without complex tracing methods, it is impossible to distinguish between the small point sources and the transfers from land. Furthermore, depending on how the septic tanks are connected, particularly some older ones, outflow may increase during rainfall so that rain does not act as a dilutor. Dilution is not seen in the concentration time series from these catchments. Nevertheless, these small point sources are a common feature in rural, agricultural areas and the net effect is a contribution to the diffuse pollution from the catchment. In periods of high flow, the proportion of TP as TRP may be lower (as in Table 5), but the TP loads are also much higher, and the increased likelihood of more intense storms is likely to push the concentration duration curve higher, possibly out of one band into one of lower WFD status. This will clearly have important implications for compliance with water quality targets.

3.6. Estimating future phosphorus transfers

The strong relationship between event rainfall and event TP load for Newby Beck (Fig. 9), i.e.

$$\text{Event TP load} = (2.50 \pm 0.27)\ \text{Event rain total} + (-11.56 \pm 6.72) \qquad \left(R^2 = 0.90\right) \tag{3}$$

was combined with the frequency of rainfall events from the UKCP09 data (Fig. 4), according to Eq. (2), to estimate potential changes in phosphorus transfer in the future, related to changes in rainfall patterns only. Only rainfall events up to 80 mm were included, which included the 99th percentile of event size (Table 3), as the relationship in Eq. (3) was only defined up to 80 mm. This resulted in a small underestimation in the event load, but events greater than 80 mm were few in number and made a small contribution to the total event load. Table 7 indicates that, from changes in rainfall patterns alone, the median annual load from events greater than 10 mm may increase by around 9%. The uncertainty in the Event load – Event rain relationship was included by using the 5th and 95th confidence limits on the coefficients but this made only a small difference to the estimated change in Table 7 (8–10%). The inter-annual variability, which is reflected in the UKCP09 Weather Generator data, is shown by the 5th and 95th percentiles in Table 7, indicating that

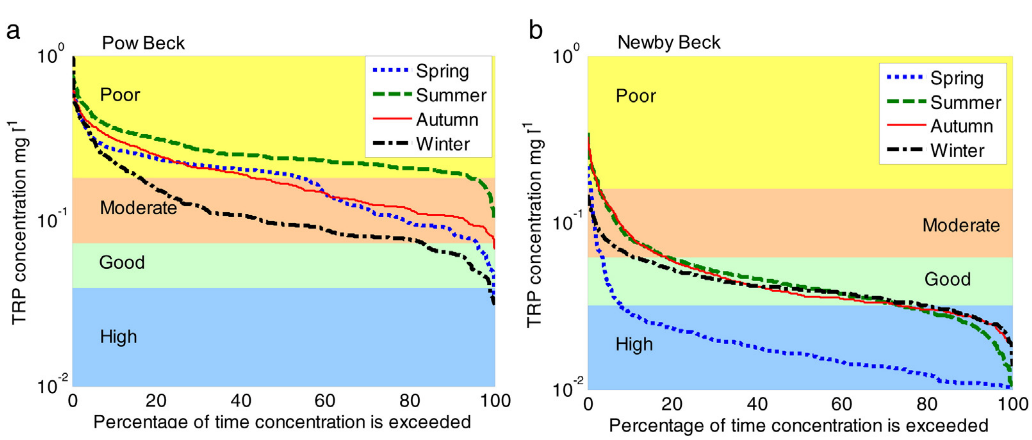

Fig. 10. Seasonal total reactive phosphorus (TRP) concentration duration curves for Pow Beck (a) and Newby Beck (b), with WFD Environmental standards for phosphorus marked as bands. Spring = MAM; Summer = JJA; Autumn = SON; Winter = DJF.

Table 7
Estimated total event loads (kg) and changes in total phosphorus (TP) load in Newby Beck transferred in events with rainfall greater than 10 mm. Use of the linear model for future rainfall projections assumes that current agricultural practices remain unchanged.

	Median load (kg)	Median load (kg) with uncertainty from Event load–Event rain relationship		5th percentile	% change from median	95th percentile	% change from median
Gradient	m = 2.50	m = 2.23	m = 2.77	m = 2.50		m = 2.50	
Intercept	c = −11.56	c = −4.76	c = −18.36	c = −11.56		c = −11.56	
Baseline	1296	1330	1263	1107	−15%	1520	+17%
2050s	1414	1441	1386	1112	−21%	1744	+23%
% change (baseline to 2050)	+9%	+8%	+10%	+0%		+15%	

the variation year by year may be larger than the projected change in median (±17% from median in baseline condition, ±23% from median in 2050s). Nevertheless, a significant increase in the median event load total is estimated using this model. Based on the data in Fig. 9, the event load total from events greater than 10 mm represents 75–80% of the total annual load. If the event loads in Table 7 are scaled up accordingly, to represent the total annual TP load, (by 1.25 if event load is 80% of annual load or 1.33 if event load is 75% of annual load), then the median baseline annual load becomes 1620 to 1724 kg. This is a reasonable estimate of the observed load in Newby Beck of 1750 kg for the observed year.

3.7. Limitations of the applied method

The applied method (methodology sequence is summarised in Supplementary Information) provides a simple estimation of potential changes in phosphorus transfers under future rainfall regimes. The method has worked well for these surface water-dominated catchments where the phosphorus transfer is heavily dominated by rainfall. However, for catchments with a larger groundwater influence, which might be seen in the time series data as a seasonal trend, or identified by Data-Based Mechanistic modelling (Young, 1998; Young, 2003) as a dominant pathway with a slower time constant (Ockenden and Chappell, 2011), it would not be possible to identify a discharge threshold for high flow events. In that case it would be preferable to use a threshold based on rate of change of discharge. In addition, the presence of slower pathways would make it more difficult to identify the start and end of events, as the damping effect of the slower pathways on the hydrograph would merge events following quickly one after the other.

The high temporal resolution nutrient data used in this method brings added insight into biogeochemical processes by providing better information on the high frequency dynamics of a system, but the equipment required is costly and time-consuming to maintain in order to avoid missing data. More than 12 months of data might provide a more robust relationship between event rainfall and TP load, but, as shown by investigation of the uncertainties in future TP transfers, the uncertainty due to errors in the rainfall-TP load relationship is considerably smaller than the uncertainty due to the inter-annual variability in rainfall. For seasonal analysis, it is important to have a full year of data (or multiples of a year) in order to avoid bias in the results.

For regions not covered by the UKCP Weather Generator, global or regional climate models (preferably ensembles of models, to account for some of the model uncertainty) can provide projections of rainfall. However, this is usually not resolved to sub-daily frequency (although very high resolution climate models show improvements in sub-daily rainfall simulation, albeit for small numbers of simulations due to computational expense (e.g. Kendon et al., 2014)), and lacks the probabilistic approach of UKCP09 which shows the distribution of inter-annual variability. In the absence of sub-daily rainfall, which is needed to identify event rainfall accurately, it is possible to use daily rainfall and daily TP loads, although this is likely to result in a rainfall-TP load relationship which is less well defined, particularly in catchments with more groundwater influence where a time lag between rainfall and response in the stream is observed. In that case, integrating rainfall and TP loads over a longer timescale (days to weeks) is likely to result in a better rainfall – TP load relationship. For similar studies, on catchments which are not as surface water-dominated as those in this study, it is important to include hydrogeological research as part of the catchment characterisation.

Use of the simple linear model for predicting potential changes in TP transfer assumes that the model will still be valid in the future. This assumes that the hydrological and biogeochemical processes remain unchanged, which may not be true. Whilst many important contributing factors (e.g. topography, geology, soil type) will stay the same, others, such as land management practices may change. Nevertheless, this simple method, using the best available high-resolution nutrient data and best available distribution of rainfall projections, indicates the sensitivity of TP transfers to projected changes in rainfall, and includes the uncertainty related to both the rainfall-TP relationship and the inter-annual variability.

4. Conclusion

In this study, we have identified two features in the high temporal resolution data, which are likely to be enhanced by climate change:

- More than 90% of the suspended sediment, 80% of the TP and 70% of the TRP loads were exported from both catchments during high flows ($\geq Q_{10}$). With climate change expected to increase the volume of winter rainfall and the intensity of rainfall events (mainly in winter but potentially in summer too), this is likely to enhance the (already disproportionally large) contribution of these high flow events to the annual loads.
- High concentrations of TRP (high enough to be classified as WFD 'poor' status) were recorded most often in the summer months, and particularly in Pow Beck, which is thought to have more (or better connected) point source inputs. Whilst it is not possible without complex tracing techniques to distinguish between small, unidentified, point source inputs and transfers from soil, the net effect of these commonly-occurring sources in rural, agricultural areas is an increase in P transfers. With climate change projected to bring hotter summers and more droughts, periods of low flow are likely to get longer, with a corresponding increase in the length of time that threshold concentrations (e.g. for WFD status or for ecological impairment) are exceeded. The likelihood of more extreme droughts will also affect the drying/rewetting effect of increasing the P concentration released to soil solution following drying.

There was a strong linear relationship between total event rainfall and total event TP load in both catchments. Although antecedent conditions had some effect on the relationships, the non-linear effect was small compared to the variance in event rainfall. This suggests that although there may be some source limitation of sediment-bound P, with P being flushed through by several events in quick succession, the effect is small in comparison to the total pool of P available for transfer. Using the linear relationship combined with projected rainfall event frequency suggested that TP transfers could increase by around 9% on average by the 2050s, but with large inter-annual variability.

Although only approximately 50% of the nitrate load was transferred during high flows, nitrate transfer was still dominated by rainfall events, but with a larger proportion transferred during the hydrograph recession when the flow had dropped below the high flow threshold. Thus, the climate change effects are also likely to increase nitrate loads during and following extreme storm events and to increase nitrate concentrations during low flows in summer.

Both the field data and subsequent modelling provide evidence to support our hypothesis that climate change will modify the transfer of nutrients from land to water. Although the evidence discussed herein comes from two small headwater catchments, the novel combination of components is applicable elsewhere, where suitable data is available, and the implications are relevant to most temperate, agriculturally-dominated catchments where climate change is expected to bring warmer wetter winters, hotter drier summers and more intense rainfall events. This should stimulate farmers and land managers in all those regions to engage with planning approaches to improve resilience in agricultural systems and aquatic health, such as control of soil nutrient status, soil condition or land cover.

Although a smaller percentage of the nitrate load was transferred during high flows, the nitrate transfer was still dominated by rainfall events, as can be observed in the time series data (Figs. 5 and 6) but as most of the nitrate flowing through the catchment outlets was transferred in soluble form by shallow sub-surface pathways, the response time was slower than for P, with a large proportion of the nitrate being transferred in the hydrograph recession.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.12.086.

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