A combined geochemical and hydrological approach for understanding macronutrient sources

Dan J Lapworth [a*], Daren C Gooddy [a], Flo Kent [b], Tim H E Heaton [c], Steven J Cole [d], Debbie Allen [a]

[a] British Geological Survey, Maclean Building, Wallingford, Oxfordshire, OX10 8BB, UK

[b] Environment Agency, Orchard House, Endeavour Park, Addington, West Malling, Kent, ME19 5SH, UK

[c] NERC Isotope Geosciences Laboratory, Keyworth, Nottinghamshire, NG12 5GG, UK

[d] Centre for Ecology & Hydrology, Maclean Building, Wallingford, Oxfordshire, OX10 8BB, UK

*Corresponding author, email: djla@bgs.ac.uk, Tel: +44(0)1491692327, Fax: +44(0)1491692345

Abstract

This study employed complementary geochemical techniques and distributed hydrological modelling to investigate multiple sources of catchment macronutrients and characterise their changes in contrasting storm and baseflow conditions. This approach was demonstrated for the Beult catchment in the county of Kent (England), a designated Site of Special Scientific Interest (SSSI) indentified as failing to meet water quality standards for key nutrients under the Water Framework Directive. Significant changes in nutrient stoichiometry and bioavailability are observed for surface waters under contrasting flow regimes. Soluble reactive phosphorus (SRP) concentrations are approximately twice as high during baseflow compared to high flow, while the inverse is true for particulate, colloidal and dissolved hydrolysable phosphorus, dissolved organic carbon and nitrate. N:P ratios are lower during baseflow for most surface waters impacted by diffuse sources of pollution. Fluorescence indices of dissolved organic matter (DOM) show that waste water inputs may be locally important sources of more complex low molecular weight DOM, particularly during baseflow. Nitrate N and O isotope signatures, combined with other dissolved chemical tracer's, confirm the dominance of wastewater N inputs at sites downsteam of sewerage treatment works during baseflow, with a shift towards the soil N pool in surface waters across the catchment during high flow. Distributed hydrological modelling using the Grid-to-Grid model reveal areas with the greatest runoff also export higher N and P concentrations, and hence deliver a greater flux of macronutrients, while forested areas with low nutrient concentrations reduce runoff and nutrient fluxes. During periods of high runoff, nested sampling indicates that nutrient fluxes scale with catchment area. This combined approach enables a more thorough assessment of the macronutrient sources and dynamics, better informing management options in nutrient impacted catchments.

Keywords: Macronutrients; Beult Catchment; Source identification, Organic Matter Fluorescence Wastewater, Land Use, Grid-to-Grid Modelling

1 Introduction

Carbon (C), nitrogen (N) and phosphorus (P), often referred to as macronutrients, are essential components of a healthy aquatic ecosystem (Whitehead et al., 2012). However, in recent decades anthropogenic inputs of macronutrients have caused perturbations to key macronutrient cycles, and led to widespread N and P pollution of aquatic systems (Heathwaite et al., 1996; Edwards and Withers, 2008; Neal et al., 2010). This is a global problem with implications for food production and security, water quality, as well as potential climate impacts (Meyer et al., 1999; Galloway et al., 2004).

In catchments with agricultural land use, diffuse sources usually dominate nutrient inputs to streams and groundwater, while in non-agricultural areas point sources such sewage/waste water treatment works (WWTWs) are important inputs (Johnes et al., 1996; Howarth et al., 1996; Jordan et al., 1997; Palmer-Felgate et al., 2010). The European Water Framework Directive (WFD 2000) requires that water bodies achieve good ecological and water quality status by 2015. Therefore, there is a pressing need to understand nutrient sources, transport processes and attenuation mechanisms at the catchment scale.

Phosphorus (P) is an important nutrient in the environment: too little can inhibit plant growth whilst too much can lead to an excess which is subsequently stored in the soil. This excess P can then be released into water bodies and may contribute to eutrophication and associated loss of ecological status (Jarvie et al., 2006, Holman et al., 2008, Withers and Jarvie, 2008). In a catchment, there are several different potential sources of dissolved P that can enter the river or groundwater body. Livestock farming has been shown to be an important source of nutrients from fertilisers, manure and feed concentrates (P and N) in streams (Haygarth et al., 1998, Withers and Lord, 2002). Other major sources of nutrients are from point sources such as slurry tanks (Gooddy et al., 2002), leaking septic tanks or drains (Palmer-Felgate 2010) and particularly WWTWs which are a key source of PO_4 and the soluble polyphosphates used in detergents (Neal et al., 2010).

The bioavailability of nutrients is a key issue when considering the potential ecological status of freshwater bodies. Autotrophs, which can lead to eutrophication in over-enriched waters, can only use PO_4 directly, but are also able to use organic forms of P through indirect extracellular processes (Schindler, 1974). Hence, soluble reactive P (SRP) is often used as a measure of the bioavailable portion of P in environmental studies. However, P is a highly dynamic element, with the species and bioavailability dependent on changes in biological, physical and chemical factors. For example: particulate P (PP) may release surface bound PO_4 and organic forms of P; changes in redox and pH may lead to PO_4 release or binding to mineral-organic complexes; and inputs from runoff and stormflow may dramatically alter the source and form of P over a short time period (Froelich 1988; Hur and Schlautman., 2004). Another important factor is the relative ratio of different nutrients, e.g. the N:P stoichiometry, which is important in limiting autotrophic growth (Schelske et al., 1974). P limited systems have been shown to have an increased turnover of P to compensate for the low availability.

Colloids are operationally defined as particles with diameters less than 10^{-5} m (10 m) (Stumm, 1977). An important process that has received some attention in recent years has been colloid bound P transport (e.g. Haygarth et al., 1997; Lapworth et al., 2011). This is the transport of P bound to inorganic and organic particles which cover a large range of sizes from large clay-humic-metal complexes to nanometre scale humic-like compounds and carbonate, iron or silicate fractions.

Increased anthropogenic inputs of N to the UK land surface, largely from fertiliser as well as some depositional sources, have resulted in widespread N pollution and the subsequent deterioration in the quality of both surface water and groundwater (e.g. Foster et al., 1986; MAFF 1993; Wang et al., 2012; Worrall et al., 2012). Nitrogen pollution in UK freshwaters is predominantly in the form of nitrate (NO_3) rather than nitrite (NO_2) or ammonium (NH_4) due to the predominantly oxidising conditions. Nitrate concentrations in rivers often show a distinct seasonal variation, with peak concentrations in winter months and low concentrations in summer months (Johnes and Burt, 1993).

Dissolved organic matter (DOM) includes compounds such as carbohydrates and proteins, as well as humic substances including fulvic and humic acids (Thurman, 1985). Natural organic matter is derived from the decay of organic material from both plant and animal sources and almost half of all NOM fluoresces (Senesi, 1993). Recent studies suggest that humic substances are a complex mixture of both microbial and plant biopolymers, with their various breakdown products, and cannot be classed as a distinct chemical structure (Kelleher and Simpson, 2006). In the natural environment DOM is often a complex mixture of many compounds, and as such is difficult and costly to characterise (Leenheer and Croue, 2003).

Much work has been undertaken in the last decades to quantify C, N and P concentrations and fluxes, and the nature of nutrient transformations at the catchment and continental scale (Gruber and Galloway, 2008). However, there is still a major gap in current understanding of how nutrients are retained within complex landscapes and released to surface and groundwater bodies via surface and subsurface flow pathways. Most published studies to date have tended to focus only on one or two macronutrients; studies that combine all three nutrients are rare but are required to fully understand nutrient flux and processes within aquatic ecosystems (Whitehead et al., 2012).

In this paper nutrient (C, N and P) concentrations, species, fluxes and associations with colloidal and particulate matter are investigated within the Beult catchment of southeast England, UK. The River Beult was chosen for this study as it has 'unfavourable status' as a result of failure to meet water quality targets, as well as having other chemical and biological status concerns (Environment Agency, 2005). A spatial survey of water quality across the catchment, for both groundwater and surface water, was carried out during high flow (below a return period of 10 years for the gauged site at Stile Bridge) and baseflow conditions within areas of contrasting land use, giving a snapshot of the nutrient status and mobility across the catchment.

This study uses a range of complimentary techniques to investigate nutrient processes within the catchment: (i) tangential flow fractionation (TFF) is used to investigate the association of P and C to particulate, colloidal and dissolved phases (<10 KDa), (ii) dissolved organic matter (DOM) is characterised using excitation-emission matrix (EEM) fluorescence spectroscopy to investigate the nature of both labile and recalcitrant DOM, (iii) N and O isotope techniques are used to investigate different sources of NO_3 within the catchment, (iv) coupled Grid-to-Grid distributed hydrological modelling (Bell et al., 2009; Moore et al., 2006, 2007) and nutrient chemistry data are used to explore spatial relationships between runoff and nutrient flux. This type of novel multi-technique approach enables a more thorough assessment of macronutrient sources and dynamics across the catchment, and so better informs choices of management options in nutrient impacted catchments.

2 Study area

2.1 Location, hydrology and geology

Figure 1 shows the location of the Beult catchment, simplified geology, and key population centres. The River Beult rises near Ashford, Kent, and then flows North-west through Headcorn, forming the largest tributary of the River Medway. The Beult catchment is predominantly rural with scattered settlements: total urban coverage is <1% of the total catchment area. Over 60% of the land-use is classified as agricultural (CLC, 2000). During the 1930s, the lower section of the river between Smarden and Yalding was straightened, widened and deepened to increase flow and drainage. Today, water abstraction is largely for agricultural use, and therefore temporally variable; surface water flow is increased in some reaches by effluent returns from sewage treatment works.

Temporary weirs and sluices are used upstream of Stilebridge in the summer months to maintain river stage and manage flow. Daily mean river flow for the Beult at Stile Bridge, with a catchment area of 277 km^2 (51°12′08.6584″N, 000°30′54.4021″E), is shown in Figure 2a. The Weald Clay formation covers the vast majority of the catchment area (approx. 80%, see Figure 1) and very little natural storage exists causing a flashy runoff regime. There are only minor groundwater inputs (baseflow) from the Lower Greensand Group, resulting in a baseflow index of 0.2 at Stile Bridge (NRFA, 2012).

The catchment is underlain by the Weald Clay formation, a thick (110–270m) clay and silty-clay within which are found outcrops of limestone and sand. The Lower Greensand Group, comprising the Folkstone, Sandgate, Hythe and Atherfield Clay formations, crop out along the northern margin of the catchment. The underlying

Wealden Group, the Tunbridge Wells Sand formation, and Wadhurst Clay formation, are located on the southern margin of the catchment (Figure 1). There are substantial superficial deposits of alluvium, silty and sand gravel river terrace deposits adjacent to the River Beult and its tributaries. For a detailed account of the geology of the Maidstone area see Worssam (1963). Some spring flow issues from the Lower Greensand Group, which is exposed along the northern margin of the catchments, and also from the Tunbridge Wells Sand in the south.

2.2 Water quality status of the Beult catchment

resulted in the River Beult being designated as having 'unfavourable status' and indentified as failing to meet quality standards under the WFD. High phosphate (PO_4) concentrations are the primary reason for the water quality failures, although nitrate (NO_3) concentrations are also high. The water quality at four sites, two downstream of WWTWs and two impacted by other sources, have been monitored by the Environment Agency (EA) between 2002 and 2008 for temporal trends in P and N species. Average ammonium concentrations were low for all of the monitoring sites (<0.5 mg/L), with highest concentrations during low flow periods at all sites. Long-term results for NO_3 and SRP from this water quality monitoring are included in this paper, and provide a context for the detailed follow-up work carried out during high flow and baseflow conditions.

3 Methods

3.1 Sites and sampling

Figure 1 shows the location of sites that are investigated as part of this study. A total of 20 sites from across the Beult catchment were sampled on two occasions, once during a period of high flow following intense rainfall in November 2008 and then during baseflow conditions in July 2009. The four EA monitoring sites that feature in this study are also shown. Table S1, supplementary information, shows details on site location, water type, and potential sources of nutrients.

Sites with potentially contrasting nutrient input sources were selected across the catchment based on land-use data and information on licensed discharges to the Beult. Two surface water sites that were impacted by local WWTW discharges, Sutton Valence and Biddenden, were included in this study. Twelve sites were impacted by diffuse pollution from agricultural land-use, and two sites were selected where forest/woodland was the predominant land-use. Groundwater samples were collected at three locations from springs that issue at the contact between the Lower Greensand and the Weald Clay formations to the north of the catchment.

Groundwater sites were located to the north of the catchment. The sewage impacted sites were sampled downstream of discharges from the Sutton Valence WWTW, to the northwest of the catchment and downstream of Biddenden WWTW in its southern part. Samples upstream of the Sutton Valence WWTW were also collected for comparison. Agriculturally impacted sites, including field drains, were sampled from the River Sherway, a tributary of the River Beult. Two sites with predominantly forested land-use were located in the southern part of the catchment (see Figure 1), and represent nutrient water quality for parts of the catchment that have been unaffected by either agricultural or wastewater inputs.

River samples were collected using a bucket; samples were taken from the centre of the flowing watercourse. Care was taken to ensure that the inlet did not disturb river bed sediment during sampling. Groundwater samples were collected from springs taking care to obtain samples from close to the inlet of collection tanks. On-site water quality variables - dissolved oxygen (DO), pH, redox potential temperature and specific electrical conductance (SEC) - were measured and allowed to stabilise prior to sampling where appropriate. DO, pH and redox potential were measured in a flow-through cell to obtain a representative field value. Alkalinity, referred to as HCO_3 in this paper, was determined in the field using 50 mL of sample by titration against 1.6N sulphuric acid. The average values from two repeat titrations obtained in the field were reported.

Samples for inorganic analysis were filtered in the field using 0.45 m cellulose nitrate filters (Whatman™). Samples for DOC were filtered through a 0.45 µm silver filters (Millipore™) into sterile acid-washed glass containers and stored refrigerated in the dark at 4º C. A 2 litre unfiltered sample was collected and stored in dark plastic bottles for analysis of the $^{15}N/^{14}N$) and oxygen ($^{18}O/^{16}O$) isotope ratios of nitrate.

3.2 Tangential Flow Fractionation

The use of Tangential-Flow Fractionation (TFF) has been investigated as an improved method for fractionation of colloidal material (Guéguen et al., 2002; Morrison and Benoit, 2004), as the tangential arrangement minimises the clogging at the membrane surface. Although this is better than the classical method of filtration it does not avoid coagulation altogether. Previous work by Lapworth et al. (2009a and 2011) has successfully used this method to investigate P and DOM association with different size fractions in surface and groundwaters. The mass balance recovery of P was calculated for all samples and was found to vary between 89 and 102% for P, and was slightly lower for DOC (72 to 86%) presumably due to adsorption effects on the filter membrane.

A Pellicon 2 Millipore™ system was used for TFF with a range of large surface area composite regenerated cellulose filters (nominal cut-off 10 kDa). A thorough protocol for cleaning membranes is required (Guéguen et al., 2002), and was followed for this work. All samples were pre-filtered prior to the TFF treatment to remove the larger particulate matter using Whatman ® glass fibre filters (nominal cut-off 2.7 m). An unfiltered sample was collected and stored in acid-washed glass bottles for analysis of the whole sample. The full suite of filters were used in the initial round sampled under high flow conditions to investigate the association of P with different sample fractions. TFF using the nominal 10 KDa filter, representing the truly dissolved phase, was carried out for a subset of seven sites of contrasting land-use during both high and low flow conditions.

3.3 Chemical analysis

3.3.1 Inorganic Chemistry

Soluble reactive P (SRP) is a measure of the inorganic monomeric and easily-hydrolysable phosphorus in the sample that has been filtered through a 0.45 m filter. The SRP was determined colorimetrically using the method of Murphy and Riley (1962) as modified by Neal et al. (2000). Total phosphorus (TP) is the combination of total dissolved P and particulate P; this was measured by the method of Eisenreich et al. (1975). Total dissolved P (TDP) was determined using the method of Eisenreich et al. (1975) after filtration through a 0.45 m cellulose filter. The dissolved poorly-hydrolysable P (DHP) was calculated by difference. DP, the 'truly' dissolved P was isolated by TFF (10 KDa) and P determined using the Eisenreich et al. (1975) method. Colloidal P (CP) is operationally defined as <0.45 mm and >10 KDa and was calculated by difference. Major anions (NO_3-N, SO_4 and Cl) were analysed by Dionex ™ liquid chromatography on filtered (0.45 m) samples. HCO_3, pH and specific electrical conductance (SEC), and DO were determined in the field. P analysis was carried out within a week of sampling. A breakdown of P analysis used in this study is shown in the electronic supplementary information (Table S2). Limits of detection (LOD) for the P species were 7 g/L, LODs for the other analytes were as follows: DOC (0.5 mg/L), NO_3-N SO_4 and Cl (0.1 mg/L), HCO_3 (5 mg/L).

3.3.2 ^{15}N and ^{18}O NO_3 analysis

Nitrate was separated on anion resins and prepared as silver nitrate for analysis of $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios by oxidative combustion and high-temperature pyrolysis, respectively, in Thermo Finnigan (Bremen, Germany) Flash 1112 and TC elemental analysers linked to a Delta+ XL mass spectrometer (Silva et al., 2000; Heaton et al., 2004). Isotope ratios were calculated as ^{15}N values versus atmospheric N_2 and ^{18}O values versus SMOW by comparison with IAEA standards N-1, N-2, and NO-3. Analytical precision (1 SD) was typically <0.3‰ for ^{15}N and <0.6‰ for ^{18}O.

3.3.3 Organic matter characterisation

Dissolved organic carbon (DOC) was measured using a Thermalox™ C analyser after acidification and sparging, for both sampling rounds. In addition, organic matter fluorescence analysis was carried out to investigate the changes in dissolved organic matter characteristics for selected sites in both sampling rounds following TFF (<10 KDa).

Fluorescence spectroscopy has been used in many studies to characterise and understand the sources of DOM in wastewater, surface water, groundwater and terrestrial ecosystems (Baker, 2001, 2002; Lapworth et al., 2008, 2009a). Florescence indices of DOM structure can provide information on key characteristics of DOM, including the degree of humification, differentiating microbial and terrestrial sources and the degree of structural conjugation and aromaticity (Zolsay et al., 1999; McKnight et al., 2001).

All organic matter fluorescence analysis was carried out within a week of sampling. Samples were stored in glass vials in the dark at 4°C, and allowed to equilibrate to 20°C prior to analysis. A Varian™ Cary Eclipse fluorescence spectrometer was used for the fluorescence analysis. Excitation (Ex) wavelengths were set between 200 and 400 nm with a 5 nm bandwidth and emission (Em) wavelength were set between 250 and 500 nm with a 2 nm bandwidth. The PMT voltage was set to 700 V, and all analysis was carried out in quartz vials with a path length of 1 cm. All fluorescence results are reported as an average of three repeat analyses, following blank subtraction, and are presented in Raman units (R.U), normalised to the area under the water Raman peak of Ultrapure water blanks at Ex350nm–Em397nm. Ultraviolet absorbance measurements (A254nm) were carried out using a Varian (UV/visible) spectrophotometer with a cell path of 1cm. Due to the high DOC (>5 mg/L) in several samples, dilution was required prior to fluorescence analysis to minimise absorbance effects. Ultrapure water (ASTM type I reagent grade water, including a UV cracker) was used for blank samples and to clean the quartz cell between samples.

Three fluorescence organic matter (FOM) peaks within the EEM were used in this study to compare intensities between sites, and sampling rounds: the fulvic-like (FA) maxima (Ex330–340 nm, Em410–460 nm), the tryptophan-like (TRP) maxima (Ex270nm–290nm, Em320–360nm) and the tyrosine-like (TY) maximum (Ex280nm–270nm, Em294-302nm).

DOM characteristics were investigated through the use of three indices which have been shown to relate to DOM structure: (i) the fluorescence index (FI) which is commonly used to differentiate between terrestrial and microbial DOM sources (McKnight et al., 2001), (ii) the humification index (HI), an indication of humicity, and the condensing of fluorescing molecules (Zsolnay et al., 2001), (iii) the ratio of two fluorescing components( ), representing recent labile OM, and representing recalcitrant OM (Wilson and Xenopoulos., 2009; Parlanti et al., 2000). Data was processed and indices calculated using R software (Lapworth and Kinniburgh, 2009).

3.3.4 Mineralogy of suspended material

X-ray diffraction (XRD) analysis was carried out on the fine fraction (<2 m) of suspended material from five river samples, to characterise the mineralogy of this material during the high flow survey. Analytical details and a summary table of results are presented in the electronic supplementary information (Table S4).

3.4 Modelling runoff contributions across the catchment

The hydrological model used in this study was the Grid-to-Grid (G2G) Model (Bell et al., 2009; Moore et al., 2006, 2007) which is a distributed grid-based rainfall-runoff and routing model. It was developed as a means of modelling “everywhere” through use of an area-wide approach that provides a natural way of addressing the ungauged hydrological forecasting problem (i.e. locations where observed flows are not available). The distributed form of G2G means that modelled flows are sensitive to both the storm pattern and landscape shaping (through use of supporting spatial datasets on terrain, soil/geology and land-cover), allowing unusual and extreme floods to be better simulated through capturing the spatio-temporal evolution of river flows across the model domain (Cole and Moore, 2009; Moore et al., 2006).

G2G is used operationally by the Flood Forecasting Centre (FFC) over England & Wales (Price et al., 2012) and the Scottish Flood Forecasting Service over Scotland (Cranston et al., 2012) to support national Flood Guidance Statements. The FFC countrywide configuration of the G2G Model, which runs on a 1km grid with a 15 minute time-step, is used in this study. Gridded rainfall inputs to the model are formed from the national network of EA tipping-bucket raingauges using multiquadric surface fitting techniques (Moore et al., 2004; Cole and Moore, 2008) with automated quality-control applied to the raingauge records (Howard et al., 2012).

In this study, the G2G Model has been used for the high flow monitoring survey. Modelled flows have been extracted for grid-cells that correspond to the sample locations and aggregated runoff volumes mapped across the domain to understand the contribution to runoff and river flow from different parts of the Beult catchment.

4 Results

4.1 Historical changes in PO_4 and NO_3 between 2002 and 2008

Figure 2b, 2c and 2d show the temporal variations for NO_3-N, SRP-P and molar N:P at the four long-term monitoring sites within the Beult catchment. Two sites, Biddenden and Sutton Valence-ds, are situated downstream of sewage treatment inputs, and the other two sites, Romden Castle and Franks Bridge, do not have significant upstream inputs from WWTW.

Overall, the sites with WWTW inputs show higher mean SRP and NO_3 concentrations compared to sites without sewage inputs (see Figure 2b and 2c). Mean concentrations of SRP g/L) and NO_3-N (mg/L) are 194 and 4.1 (Romden Castle), 227 and 7.4 (Franks Bridge), 639 and 12 (Biddenden-ds), 2034 and 19.7 (Sutton Valence-ds). Mean concentrations for SRP and NO_3-N at Sutton Valence-ds> Biddenden-ds > Franks Bridge> Romden Castle, and sites downstream of WWTW discharges also show the greatest variations (Figure 2b-d).

The temporal trends for NO_3 at the four long-term sites show less similarity based on the historical time-series data between 2003 and 2008 (Figure 2b). At the Sutton Valence site there is an overall increase in concentration, and the highest concentrations are found in periods of low flow. At Franks Bridge and Biddenden, while higher concentrations are also generally found during periods of low flow, and when temperatures are higher, there is no obvious long-term change in mean annual concentrations. At Romden Castle the temporal trend is less distinct, although there is still considerable variation. At Romden Castle NO_3-N concentrations are usually below the EU drinking water limit of 11.3 mg/L, while concentrations are consistently above this water quality limit at the other sites.

The highest SRP concentrations (Figure 2c) are found during the periods of low flow for all four sites. SRP-P concentrations at both WWTW impacted sites are regularly >1000 g/L throughout the monitoring period. Figure 2c shows that there is a marked decrease in SRP concentrations during spring 2004 at the Sutton Valence site, and concentrations are now comparable with the Biddenden site, also downstream of a WWTW. This sudden decrease in SRP concentration, and increase in N:P (Figure 2), at Sutton Valance coincides with the use of reed-beds at this site as part of a water treatment upgrade for P stripping.

4.2 Inorganic and nutrient chemistry

Table 1 shows results for key nutrient species (DOC, NO_3, TDP, SRP, DHP, TP, PP and ratios of NO_3:SRP, SRP:DHP, NO_3:Cl TDP:Cl and SRP:Cl), for twenty sites across the Beult catchment. Results for both high flow (R1) and baseflow (R2) conditions are presented. All nitrate concentrations are expressed as N (mg/L). Table S3, electronic supplementary information, shows results for selected chemical parameters: pH, SEC, HCO_3, SO_4, Cl. Figure 3 shows a ternary plot of key nutrients: DOC, SRP and NO_3 for the different land-use types during both sampling rounds.

Analysis of variance (ANOVA) was used to explore the differences in variable concentrations (pH, SEC, HCO_3, SO_4, Cl, DOC, NO_3, TDP, SRP and DHP) both between different types of water and between the two sampling rounds. Values were $\log_{(10)}$ transformed prior to ANOVA and results are shown in Table 2. Significant differences ($p<0.05$) in all variables are found between the different sources (i.e. springs, field drains etc) as well as between the two sampling rounds with the exception of SO_4 and DHP.

Groundwater from springs were found to have low concentrations of all P species, and high SEC and concentrations of NO_3, compared to most surface waters and all waste water impacted sites. River samples from the two sites with dominantly forested land-use had the lowest average SEC, NO_3 and dissolved P concentrations of any group, including the springs. These two sites had contrasting PP concentrations, which accounts for a significant proportion (>50%) of TP at both sites. Sites impacted by WWTW have NO_3 concentrations <10 mg/L, and higher mean SRP and TDP concentrations compared to those sites where agricultural land-use dominated.

The SRP:DHP ratio was either greater for the baseflow survey or showed no change for the majority of sites, with the exception of Sutton Valance WWTW, Snapmill and

Little Ommerden, two agriculturally impacted sites. In many cases the %DHP was twice as high during the high flow conditions compared to baseflow.

Considerably higher concentrations of HCO_3, Cl, and dissolved P species were found during the baseflow survey for most surface waters. In contrast, NO_3, PP, SO_4 and DOC concentrations were lower at many sites during the baseflow survey. The chemistry of the springs did not vary significantly during the study, with perhaps the exception of moderately higher dissolved P, NO_3 and DOC during the high flow survey at Pope Hall Spring (Table 1). The field drains had lower mean baseflow TDP, SRP and DHP, similar DOC and higher NO_3 concentrations, compared to the agriculturally impacted rivers. However, PP concentrations were greater in the agriculturally impacted rivers compared to the field drains during both surveys. Mean NO_3 data were similar for both groups if values from Little Southernden were excluded from the analysis, which was not unreasonable as this site was clearly an outlier having the highest concentrations across the whole survey (51 mg/L-N) which did not vary between the two surveys (Table 1).

Molar NO_3:SRP ratios showed considerable variation between sites and between survey (Table 1). In the high flow survey NO_3:SRP ratios were found to be greatest for springs>field drains>forested>Agriculturally impacted>WWTW impacted, while in the baseflow survey WWTW>Agriculturally impacted sites. NO_3:SRP ratios for springs and sites that were impacted by WWTW showed the least change between the two surveys, while agriculturally impacted sites, field drains and forested sites showed the greatest changes with significantly lower ratios ($p<0.001$) during the baseflow survey. This is due to a combination of both lower NO_3 and higher SRP concentrations during baseflow. The results from the two surveys suggest that the long-term trends of lower NO_3:SRP ratios during periods of low flow compared to high flow (see Figure 2) represent processes that are occurring more widely across the catchment.

The results from the two surveys are summarised in Figure 3 using a ternary plot of DOC, NO_3 and SRP. This illustrates several key results: (i) the change in nutrient stoichiometry in surface waters due to inputs from diffuse agricultural land use and WWTW point sources, (ii) the changes in nutrient stoichiometry in WWTW and agriculturally impacted surface waters during contrasting flow conditions, (iii) the relative stability of end members from groundwater, and particularly forested sub-catchments.

4.3 Colloidal and particulate P

Figure 4 summarises the changes in P composition (PP, CP and DP) for six sites between sampling rounds. Overall, the spring sample (Knowle Game Farm) showed no significant changes in DP between the two surveys. The proportion and concentration of PP and CP was greater for most of the river sites (Sherway Bridge, Franks Bridge and the Sutton Valance sites) during the high flow conditions (Figure 4a). DP concentrations and proportions were significantly higher during the baseflow survey (Figure 4b), accounting for more than 50% TP at all sites.

Colloidal P was found to be an important proportion of TP at the Field Drain site and the site upstream of the WWTW, which showed the highest concentration of TP as well as DP of any site, even during baseflow. There were dramatic changes in P composition at the Sutton Valence site, downstream of WWTW inputs, during baseflow. At this location, there appears to be a significant source of P upstream of the WWTW, which the treated effluent was actually diluting during both surveys. The concentration of WWTW SRP-P inputs was significantly lower during the high flow conditions (260 g/L compared to 928 g/L), presumably due to dilution from rainfall (Table 1). The downstream composition at Sutton Valence is clearly dominated by the WWTW inputs during baseflow conditions (Figure 4b), due to very low natural river flow. The similarities in inorganic chemistry are noticeable during the baseflow survey (see Table 1).

XRD analysis indicates that the suspended sediment samples have similar mineralogies with major amounts of quartz, minor illite/smectite, ‘kaolin’ (one of the kaolin group minerals including halloysite, kaolinite etc.) and ‘mica’ (undifferentiated mica species possibly including muscovite, biotite, illite) and trace amounts of K-feldspar and calcite (Table S4). There was no evidence of calcite in the field drain sample.

4.4 Fluorescence DOM characteristics

Table 3 shows the results for selected dissolved organic matter indices (TFF<10 KDa), for six sites sampled during both surveys. The spring site showed no significant changes in DOM character for the two surveys, indicative of a stable structural composition of DOM, even during extreme rainfall events. The other sites showed marked decreases in FA-like, TRP-like, TY-like fluorescence and HI during the baseflow survey. This shows the relatively high concentrations of both bioavailable (TRP and TY-like) and more recalcitrant (FA-like) DOM from the rapid overland inputs from the soil zone during high flow conditions.

For the river samples, the marked difference in HI between the two surveys suggests contrasting sources of DOM, with lower structural complexity during baseflow conditions compared to high flow conditions, suggesting more recalcitrant sources of DOM. The average FI of 1.56 is strongly indicative of terrestrially derived fulvic-like

DOM (McKnight et al., 2001), while the consistently higher FI's during the baseflow survey does perhaps suggest a larger proportion of microbial DOM during this period. In addition, the higher at the spring site, and upstream and downstream of the WWTW during the baseflow survey, also suggests a shift in DOM character to be more autochthonous, from in-situ microbially derived sources (Table 3). The shift in FI downstream of the WWTW, and consistent signature in this reach irrespective of flow conditions, perhaps indicates a consistent input of microbial derived DOM from the WWTW.

4.5 ^{15}N and ^{18}O isotopes of NO_3

Figure 5a shows a cross plot of ^{15}N and ^{18}O for NO_3 in a spring, four agriculturally impacted sites, two sites impacted by WWTW as well as the two WWTW discharge waters. The WWTW discharge was only sampled during baseflow conditions. A cross plot for ^{15}N and NO_3 for the same samples is shown in Figure 5b. Open symbols are results from the baseflow survey, filled symbols results from the high flow survey.

The isotopic composition of nitrate at the spring site (Knowle Game Farm) showed little change between the high flow and baseflow surveys. The average ^{15}N value of about +4.9‰ is typical for UK groundwater (Heaton et al., 2005); and the average ^{18}O value of +2.9‰ exactly matches the value which would be expected for bacterially-produced nitrate if one third of its oxygen is derived from water oxygen (Knowle Game Farm spring water ^{18}O = -7‰), and two thirds is from atmospheric O_2 (+24 ‰; Kendall et al., 2007). The nitrate in the spring water is ultimately derived from soils in the recharge area, and we would expect soil-derived nitrate in the catchment to have broadly similar values.

In contrast, samples of discharge from the two WWTW (which were only sampled during the baseflow survey) have both higher ^{15}N (+12.0 and +17.6‰) and slightly higher ^{18}O values (+6.1 and +7.7‰). These values conform to data published for discharge from other sewage treatment works (Anisfeld et al., 2007; Vane et al., 2007), where preferential removal of the lighter ^{14}N and ^{16}O molecules during ammonia volatilisation or denitrification result in elevated ^{15}N and ^{18}O values in residual nitrate in the discharge. Elevated ^{18}O values may also be found in fertilizer nitrate and in rainfall (though the latter can be excluded from consideration here by its low concentration), but these sources tend to have low ^{15}N values (Curtis et al., 2012; Heaton et al., 2012)

^{15}N and ^{18}O values for nitrate in most of the river waters fall within the range encompassed by groundwater or soil-derived nitrate and WWTW nitrate sources (Figure 5a). For the agriculturally impacted river sites it is evident that whilst there were large differences between their nitrate concentrations in high flow and baseflow periods, there was little difference in their isotope compositions. Differences were found, however, for the WWTW impacted sites. During baseflow the nitrate isotope compositions and concentrations of the sites downstream of the WWTWs are similar to those of the WWTW discharge, confirming the dominance of this source during baseflow. This association is absent during high flow, however, where lower ^{15}N and ^{18}O values for sites downstream of the WWTWs suggest a greater proportion of soil-derived nitrate.

4.6 Mapping runoff and nutrient flux in the Buelt during the high flow survey

Hydrographs of the G2G modelled flow during the high flow survey period are presented in Figure 6 for selected sample sites. Gauged river flows for the Beult at Romden Castle are also provided for comparison. Since these observations were not used in the G2G model configuration they provide an independent assessment of the ungauged performance of G2G. The good agreement at Romden Castle during this period gives confidence that G2G may provide meaningful flow estimates at other ungauged sample locations, particularly in terms of timing of flow peaks.

To aid understanding of the rainfall dynamics and resulting model response, catchment average rainfall and modelled soil moisture deficit (SMD) are also shown for the Romden Castle catchment (top plots, Figure 6). This identifies two distinct rainfall periods which correspond to the two observed flow peaks at Romden Castle and are marked in Figure 6. The first period is a single storm with estimated catchment average rainfall of 6.8mm in 4 hours (average 1.7mm/hr). The second period is longer and consists of three individual rainfall storms crossing the catchment which are generally less intense than the first period and give an estimated catchment average rainfall of 20.2mm in 18 hours (average 1.1mm/hr).

Maps of the time-averaged runoff ratio (runoff divided by rainfall) for each grid square derived from G2G modelling over the two storm events are shown in Figure 7 along with flux results for DOC, SRP and NO_3. The spatial heterogeneity in G2G runoff ratio provides an insight into the runoff generation across the catchment and is a reflection of the following model processes and datasets that support the G2G formulation: (i) geology – moderate permeability of the sand formations in the southwest increases recharge and lowers runoff relative to the impermeable clay that dominates elsewhere (see Figure 1); (ii) soil HOST (Hydrology of Soil Type) class

(Boorman et al., 1995) – mainly HOST class 25 overlies the impermeable clays which enhances runoff, a small area of class 18 to the southwest with lower runoff, and class 9 in lower reaches where groundwater frequently rises to within 40cm of the surface; (iii) Slope – increased runoff from steep slopes, particularly the steep scarp slope to the northeast (see Figure 1); and (iv) capturing the antecedent soil moisture conditions through the continual water accounting of the model. The relationship between modelled flux and catchment area for DOC, NO_3-N, SRP and DHP are shown in Figure 8.

5 Discussion

5.1 Macronutrient sources and concentrations

Streams draining forested parts of the catchment, while only representing a low proportion of total land-use (<10%), provide the lowest concentrations of P and N inputs to the Beult. These sites did not exceed NO_3-N or SRP-P water quality criteria (11.3 mg/L and 100 g/L) for samples collected as part of this study. All the other surface water sites in this study exceeded the SRP quality limit on at least one occasion.

Groundwater sources were shown to provide a stable and low input of P and C within the Beult catchment, but have consistently high NO_3 concentrations. Groundwater DOM fluorescence characteristics are consistent with other UK groundwater areas with agricultural land-use (Lapworth et al., 2008; 2009). These are due to a combination of factors: the relatively conservative transport of NO_3 in groundwater, the attenuation of PO_4 in the soil and aquifer, and the microbial breakdown of DOM in the soil and unsaturated zone and their long groundwater residence times compared to other waters. While the groundwater contribution to river flow in the Beult is low

(BFI = 0.2), the high concentrations of NO_3-N (ca. 15 mg/L) and high bioavailability of groundwater P (largely SRP) suggests that groundwater inputs may be ecologically significant, particularly during baseflow (Holman et al., 2008; Lapworth et al., 2011).

The nutrient composition of field drains is comparable with that of agriculturally impacted rivers, into which they drain. These can be characterised as having, on average, high concentrations of DOC (>15 mg/L), NO_3-N (>8 mg/L) and TP (>400 g/L) during high flow, and much lower DOC (ca.10mg/L) and NO_3-N (<1 mg/L) during baseflow (excluding the anomalously high result from site 7). The shift in HI in the surface waters shows that there is an important change in DOM character as well as the abundance during contrasting flow conditions (Conran et al., 1999; Hood et al., 2006). Under high flow, the surface waters of the Beult catchment are enriched with a DOM of higher complexity as well as more abundant sources of bioavailable C, in the form of proteins, due to C export from the dominantly agricultural land-use (Conran et al., 1999). The values (ca. 0.6) are consistent with other studies for catchments with a high proportion of agricultural land-use (Wilson and Xenopoulos 2009).

SRP concentrations were noticeably less for the majority of field drain sites during the baseflow survey (see Table 1), while they were greater for the agriculturally impacted rivers. This suggests either (i) greater potential for P attenuation or a greater proportion of shallow groundwater in field drain sources during baseflow, or (ii) perhaps other important sources of SRP within the agriculturally dominated catchment such as septic tanks (Palmer-Felgate et al., 2010). In-stream and hyporheic zone uptake during baseflow conditions has been widely reported as an important mechanism for P attenuation in surface waters (Mulholland et al., 1997; Jarvie et al., 2006). River CP and PP concentrations and proportions were found to be greater during high flow periods compared to low flow periods, presumably due to the mobilisation of decomposing mineral and organic P sources in leaf litter and river bed sediment as a result of the increase in hydrological energy (Haygarth et al., 2005). The site upstream of the WWTW had the highest SRP concentrations during both high and baseflow conditions: 430 and 1252 g/L respectively (Table 1). This is downstream of a dairy farm, which can contain important sources of TDP, in part due to rapid runoff to surface water from areas of hard standing (Hively et al., 2005).

WWTW impacted sites have lower DOM concentrations compared to those from agriculturally impacted sources, but NO_3 and SRP concentrations are significantly higher compared to other groups during baseflow conditions (Figure 3). Average NO3-N concentrations were 8.8 and 29 mg/L for WWTW impacted sites during the high and low flow survey respectively. At the Sutton Valance site, although WWTW inputs actually improved the water quality with respect to P, SRP-P concentrations are still very high (349-912 g/L), and the inorganic chemistry suggests that the stream is composed of a significant proportion (perhaps as high as 80%) of treated water during baseflow conditions.

The shift in FOM indices (and HI) downstream of the WWTW indicates a more microbial source of DOM (see Table 3). The higher   and lower HI found at the site downstream of the WWTWs, compared to the agriculturally impacted sites, also means that WW inputs may be locally important sources of more complex DOM, particularly during baseflow (Imai et al., 2002).

Nitrate N and O isotopes signatures, combined with other chemical tracers (e.g. NO_3, SRP, Cl), confirm the dominance of WWTW N inputs at sites down-steam of WWTW during baseflow (Curt et al., 2004). During high flow the nitrate isotope signature is shifted towards the soil N pool for all surface water sites, suggesting that this, i.e. diffuse agricultural sources, is the dominant source N across the catchment during these conditions (Neal et al., 2008).

Sites that were impacted by diffuse pollution from agriculture showed no net change in ^{15}N during contrasting flow conditions, with the exception of one site upstream of Sutton Valence which is shifted to higher values (in excess of 17) during baseflow. This illustrates two processes: (i) a relatively stable N source from agricultural catchments, probably derived from the soil N pool, and (ii) the importance of point sources of N, in this case perhaps indicative of a manure source of N (Wassenaar, 1995; Choi et al., 2007). This could be from a dairy farm upstream and in close proximity to the site. The combined uses of geochemistry and isotopes have helped identify the different N pools, and the complex temporal dynamics and relative dominance of these pools originating from different sources within the catchment.

5.2 Spatial variations in runoff and nutrient fluxes

Modelled runoff ratio across the catchment shows a large degree of spatial heterogeneity for the high flow survey periods (Figure 7). The southwest of the catchment shows a lower runoff ratio as well as significantly lower nutrient concentrations and fluxes. This is a result of the soil, geological and topographical controls on modelled runoff as well as the wooded land-use. These contrast with the higher runoff and nutrient concentrations and fluxes in the centre and north of the catchment, which are hotspots for nutrient export to the Beult. There is a consistent relationship between DOC, NO_3-N and SRP fluxes at six selected sample sites during the first event (see Figures 7a, c and e), and it is clear from Figure 8 (filled circles) that these fluxes scale linearly with catchment size. Linear regression using data from the first event give coefficient of determination values between 0.995-0.985 for the six flux/catchment area relationships shown in Figure 8. The strong relationships found between all chemical fluxes and catchment size is a surprising result given the potential errors associated with the modelling, sampling and analysis, but perhaps provides a measure of confidence in the point flow estimates generated from the G2G hydrological model. The relationship is poorer, as would be expected, for smaller catchments and lower fluxes, due to larger uncertainties in the modelling. Given the high flow/runoff conditions, this suggests that at the selected sample sites the nutrient fluxes from this event are dominated by diffuse surface runoff sources, which are evenly distributed across these sub-catchments and mask out any point source inputs.

The response to the second larger event (see Figure 6) is different, both in terms of spatial flux patterns (see Figure 7) and the slope of flux-catchment size relationships for all the nutrients based on three sample sites (Figure 8, hollow squares). An exception is the conservative tracer Cl (Figure 8f) where the flux-catchment relationship holds over both events as might be expected since catchment inputs are dominated by rainfall sources (Figure 8f). These results could be explained in terms of spatial differences in runoff ratio, with proportionally higher catchment runoff ratio values as well as the magnitude of the second event. The higher magnitude event mobilised greater DOC, TDP, SRP and particularly DHP (see Figure 8e) from the soil for a given catchment area. In contrast, the more conservative (unbound) pollutant NO_3 shows a reduction in flux during the higher magnitude runoff event: this is most likely due to the proportionally higher runoff ratio for this event and subcatchment (see Figure 7b). This is also corroborated by the lower NO_3 concentrations at these sites and lower molar N:P ratios compared to the sites sampled during the first event (see Table 1). The apparent loss of P flux downstream of site 9 (Figure 7f) may reflect the sample timing at site 9 and the fact that this site was sampled a day later on the falling rather than rising hydrograph limb of the event as was the case for the two downstream sites (see Figure 6). This is consistent with a "clockwise" solute hysteresis effect during storm events where higher concentrations are observed during the hydrograph rising limb of an event compared with those measured on the falling limb (House and Warwick, 1998). This combined approach using a distributed hydrological model and hydrochemical sampling shows good potential for evaluating how different nutrient fluxes and pools respond temporally and spatially depending on antecedent conditions and changes in catchment runoff characteristics. Such an approach could help inform catchment-based water quality management plans for reducing and understanding diffuse and point source pollution for the River Beult and elsewhere, particularly as the G2G Model is already configured for England, Wales and Scotland.

5.3 Macronutrient bioavailability under contrasting flow conditions

Within the Beult catchment there are significant changes in nutrient bioavailability and stoichiometry for surface waters during baseflow and high flow conditions following intense rainfall. SRP concentrations are approximately twice as high during baseflow compared to high flow, while the inverse is true for PP, CP and DHP and DOC and NO_3.

Overall, N:P ratios are lower during baseflow for most surface waters that are impacted by diffuse sources pollution (Table 1 and Figure 2). If N and P values are normalised using Cl, a conservative tracer with respect to the potential evaporation and rainfall inputs to the hydrological model, there are no net changes in TDP and SRP between contrasting flow conditions at sites impacted by diffuse sources of pollution. However, sites impacted by WWTW are relatively enriched with respect to

TDP and SRP during baseflow (Table 1), and all surface water sites show relative depletion in NO_3, so other wastewater sources upstream of these sites such as septic tanks or dairy waste cannot be ruled out (Palmer-Felgate et al., 2010; Hively et al., 2005). At some sites (Field Drain, Sutton Valence-us, Franks Bridge, Snoadhill Farm) there are increases in SRP:Cl ratios during baseflow, possibly due to release of surface bound P from sediments under higher pH and temperatures.

TFF results also show that there is a shift in the association of P from PP towards 'truly' dissolved forms and colloidal particles during low flow conditions. These are more bioavailable forms of P, and could also be in greater abundance due to the in-stream breakdown of PP and CP, as well as other physical and chemical factors (Bostrom 1988; Furumai et al., 1989). The higher pH and temperatures during baseflow could facilitate the release of PO_4 from sediments, both bed sediments and suspended particulate and colloidal matter, due to increased completion for binding sites on ferric complexes between hydroxyl and PO_4 ions (Kim et al., 2003; Abrams and Jarrell, 1995).

The low flow rates could also result in changes in bioavailable P within the water column, shifting the N:P ratio and potential for eutrophication. Cyclical periods of high flow will be important in replenishing nutrient sources within river networks, sustaining the cycle of bioavailable P release and inputs to the catchment. They will also be important in transferring nutrients from zones of excess to zones of relative depletion. Autotrophic growth, and the potential deterioration in ecological status, is likely to be limited by N availability during baseflow, which could partly account for the relative enrichment in SRP and TDP in surface waters in this period.

There is a complex interaction between river sediments, which are largely composed of illite/smectite, kaolin and mica (Table S4, electronic supplementary information), and DOM. This is controlled by pH and major ion chemistry (Gu et al., 1994). At lower pH there is greater adsorption to clay surfaces by fulvic and humic acids, particularly of higher molecular weight (MW) fractions, and PO_4 has been shown to inhibit the adsorption of low MW DOM fractions due to competition with surface ligand exchange and electrostatic interactions (Hur and Schlautman, 2004).

The change in the DOM character within receiving rivers is partly due to inputs of lower MW hydrophilic acids from WWTW sources (Imai et al., 2002). The interplay between these multiple factors, different sources of C (natural and anthropogenic), and the combined effect of higher pH and higher PO_4, are all likely to contribute to the overall shift in DOM character during contrasting flow conditions within the catchment (Hood et al., 2006). Immediately after periods of high flow, and mobilisation of soil nutrient pools, and during baseflow when WWTW inputs are proportionally greater, autotrophic growth may be stimulated, producing temporal zones of more rapid biological growth (McClain et al., 2002; Merseburger et al., 2005).

As groundwater NO_3 concentrations are high compared to surface waters, these results confirm that baseflow groundwater inputs are low for most sites impacted by diffuse nutrient sources, perhaps with the exception of inputs of shallow groundwater sources to field drains. However, this could in part be due to the relatively long residence time within the subsurface and does not rule out the possibility of increased N inputs in the future due to the delayed arrival of increased NO_3 concentrations at the water table where unsaturated zones are deep or downward flow is slow (Wang et al., 2012).

As well as the obvious temporal variability in water quality due to changes in flow, longer term trends (Figure 2) show that water sources impacted by WWTW can have dramatic shifts in nutrient quality due to changes in the efficiency of P and N stripping (Neal et al., 2008). While over the same period, sites impacted by predominantly diffuse sources have not shown any long-term changes in nutrient chemistry. However, there is no simple or clear distinction between diffuse and point sources of pollution within the catchment: the reality is more dynamic and complex. For example, reaches with obvious point source inputs have been shown to be equally impacted by diffuse sources during high flow conditions.

6 Summary and Conclusions

The results from this catchment-wide study reflect the fact that the River Beult fails to meet water quality standards under the WFD. All surface waters in this study had SRP-P concentrations >100 g/L on at least one occasion. Average groundwater SRP-P concentrations were 36 g/L, almost three times the concentrations found in surface waters draining wooded areas. Groundwaters, and some field drains, had consistently high NO_3-N concentrations, >11.3 mg/L, as did sites downstream of WWTW during baseflow.

Overall, the nutrient chemistry within the Beult catchment is controlled by diffuse exports from arable agricultural land-use, as well as point source pollution from WWTW and dairy farms. Wooded areas provide relatively small areas of low nutrient input to the River Beult.

There were significant changes in nutrient bioavailability and stoichiometry for surface waters during baseflow and high flow conditions following intense rainfall. SRP concentrations were approximately twice as high during baseflow conditions compared to high flow conditions, while the inverse is true for PP, CP and DHP and DOC and NO_3. N:P ratios are lower during baseflow for most surface waters that are impacted by diffuse sources of pollution. Cl normalised values suggest that changes in

P are largely due to evaporative/dilution effects in catchments impacted by diffuse pollution, while those impacted by WWTW sources showed net enrichments in P during baseflow.

The higher FI, and lower HI found at the site downstream of the WWTWs, compared to the agriculturally impacted sites, also mean that WW inputs may be locally important sources of more complex DOM, particularly during baseflow. This is likely due to inputs of lower MW hydrophilic acids from WW sources.

N and O isotopes signatures, combined with other chemical tracers (e.g. NO_3), confirm the dominance of WWTW N inputs at sites downsteam of WWTW during baseflow conditions. During high flow the nitrate isotope signature is shifted towards the soil N pool for all surface water sites, suggesting that diffuse sources of N dominate during these conditions.

The combined use of different methods: P speciation, TFF, organic matter florescence and N and O isotope analysis of NO_3 and distributed hydrological modelling using the G2G model has helped to characterise the highly dynamic nature of nutrient sources, pollution and bioavailability in this typical lowland clay catchment. Future applications of ^{18}O-PO4 methods (e.g. Li et al., 2011) may further our understanding of P sources, fate and turnover within catchments. Given the dynamic nature of these and other catchments, long-term high-resolution monitoring of nutrients within such catchments (Neal et al., 2012) coupled with distributed hydrological modelling appears to be a useful approach to understand changes in nutrient fluxes and process within catchments.

Acknowledgements

The authors thank Peter Williams for carrying out chemical analysis and assisting during sampling campaigns. Heather Wickham and Sarah Harman (CEH) are thanked for carrying out P analysis. Simon Kemp (BGS) is thanked for carrying out mineralogy analysis. The authors thank Marianne Stuart (BGS) and Bob Moore (CEH) for reviewing the manuscript. This paper was also improved by the two anonymous reviewers. The paper is published with the permission of the Executive Director, British Geological Survey (NERC).

References:

Abrams, M.M., Jarrell, W.M., 1995. Soil-phosphorus as a potential non-point source for elevated stream phosphorus levels. J. Environ. Qual. 24, 132–138.

Baker, A., 2002. Fluorescence properties of some farm wastes: Implications for water quality monitoring. Water Res. 36, 189–195.

Baker, A., Lamont-Black, J., 2001. Fluorescence of dissolved organic matter as a natural tracer of ground water. Ground Water 39, 745–750.

Boorman, D.B., Hollis, J.M., Lilly, A., 1995. Hydrology of soil types: a hydrologically-based classification of soil of the United Kingdom. Report No. 126, Institute of Hydrology, pp 137.

Bell, V.A, Kay, A.L., Jones, R.G., Moore, R.J, Reynard, N.S., 2009. Use of soil data in a grid-based hydrological model to estimate spatial variation in changing flood risk across the UK. J. Hydrol. 377, 335-350.

Bostrom, B., 1988 Relations between chemistry, microbial biomass and activity in sediments of a polluted vs.a nonpolluted eutrophic lake.Verh. Int. Ver. Limnol. 23, 451– 459.

Choi, W.J., Han, G.H., Lee, S.M., Yoon, K.S., Choi, S.M., Ro, H.M., 2007. Impact of land-use types on nitrate concentration and d15N in unconfined ground water in rural areas of Korea. Agric. Ecosyst. Environ. 120, 259-268.

Cole,S.J., Moore, R.J., 2009. Distributed hydrological modelling using weather radar in gauged and ungauged basins. Advances in Water Resources 32(7), 1107-1120.

Cole, S.J., Moore, R.J., 2008. Hydrological modelling using raingauge-and radar-based estimators of areal rainfall. J. Hydrol. 358(3–4), 159–181.

Conran, C.S., Piampiano, J.T., Patterson, H.H., 1999. Influence of land use and hydrology on exports of carbon and nitrogen in a Maine River Basin. J. Environ. Quality 28, 953-961.

Corine Land Cover, 2000. European land use data http://www.eea.europa.eu/data-and-maps

Cranston, M., Maxey, R., Tavendale, A., Buchanan, P., Motion, A., Cole, S., Robson, A., Moore, R.J., Minett, A., 2012. Countrywide flood forecasting in Scotland: challenges for hydrometeorological model uncertainty and prediction. In: Weather Radar and Hydrology (ed. by R.J. Moore, S.J. Cole & A.J. Illingworth) (Proc. Exeter Symp., April 2011), IAHS Publ. no. 351, 538-543, 2012.

Curt, M.D., Aguado, P., Sánchez, G., Bigeriego, M., Fernandéz, J., 2004. Nitrogen isotope ratios of synthetic and organic sources of nitrate water contamination in Spain. Water Air Soil Poll. 151, 135-142.

Curtis, C.J., Heaton, T.H.E., Simpson, G.L., Evans, C.D., Shilland, J. and Turner, S., 2012. Dominance of biologically produced nitrate in upland waters of Great Britain indicated by stable isotopes. Biogeochemistry, 11, 535-554.

Edwards, A.C., Withers, P.J.A., 2008. Transport and delivery of suspended solids, nitrogen and phosphorous from various sources to freshwaters in the UK. J. Hydrol. 350, 144-153.

Eisenreich, S.J., Bannerman, R.T., Armstrong, D.E., 1975. A simplified phosphorus analytical technique. Environ. Lett. 9, 45-53.

Environment Agency (EA)., 2005. Medway catchment abstraction management strategy. < http://publications.environment-agency.gov.uk/PDF/GESO0405BNZJ-E-E.pdf> last accessed February 2012.

Foster, S.S.D., Bridge, L.R., Geake, A.K., Lawrence, A.R., Parker, J.M., 1986. The Groundwater Nitrate Problem. BGS Hydrogeology Research Report 86/2.

Froelich, P.N., 1988. Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. Limnol. Oceanogr. 33, 649–668.

Furumai, H., Kondo, T., Ohgaki, S., 1989. Phosphorus exchange kinetics and exchangeable phosphorus forms in sediments.Water Res. 23, 685–691.

Galloway, J.N., Dentener, F.J., Capone, D.G., Boyer, E.W., Howarth, R.W., Seitzinger, S.P. et al., 2004. Nitrogen cycles: past, present and future. Biogeochem. 70, 153–226.

Gooddy, D.C., Clay, J.W., Bottrell, S.H., 2002. Redox-driven changes in pore-water chemistry of the Chalk unsaturated zone beneath unlined cattle slurry lagoons. Applied Geochem. 17, 903-921.

Gruber, N., Galloway, J.N., 2008 An earth-system perspective of the global nitrogen cycle. Nature 451, 293-296.

Gu, B., Schmitt, J., Chen, Z., Liang, L., McCarthy, J.F., 1994. Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models. Environ. Sci. Tech. 28, 38-46.

Guéguen, C., Belin, C., Dominik, J., 2002. Organic colloid separation in contrasting aquatic environments with tangential flow filtration, Water Res. 36, 1677-1684.

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

Haygarth, P.M., Warwick, M.S., House, W.A., 1997. Size distribution of colloidal molybdate reactive phosphorus in river waters and soil solution. Water Res. 31, 439-448.

Haygarth, P.M., Hepworth, L., Jarvis, S.C., 1998. Forms of phosphorus transfer in hydrological pathways from soil under grazed grassland. Eur. J. Soil Sci. 49:65– 72

Heathwaite, A.L., Johnes, P.J., Peters, N.E., 1996. Trends in nutrients and water quality. Hydrol. Proc. 10, 263-293.

Heaton, T.H.E., Wynn, P., Tye, A., 2004. Low ^{15}N/^{14}N ratios for nitrate in snow in the High Arctic (79^{o}N). Atmospheric Environ. 38, 5611-5621.

Heaton, T.H.E., Stuart, M.E., Sapiano, M. and Micallef Sultana, M.,2012. An isotope study of the sources of nitrate in Malta’s groundwater. J. Hydrology, 414-415, 244-254.

Heaton, T.H.E., Trick, J.K., Williams, G.M., 2005. Isotope and dissolved gas evidence for nitrogen attenuation in landfill leachate dispersing into a chalk aquifer. Applied Geochem 20, 933-945.

Hively, W.D., Bryant, R.B., Fahey, T.J., 2005. Phosphorus concentration in overland flow from diverse locations on a New York dairy farm. J. Env. Qual. 34, 1224-1233.

Holman, I.P., Whelan, M.J., Howden, N.J.K., Bellamy, P.H., Willby, N.J., Rivas-Casado, M., McConvey, P., 2008. Phosphorus in groundwater-an overlooked contributor to eutrophication? Hydrol. Proc. 22, 5121-5127.

Hood, E., Gooseff, M.N., Johnson, S.L., 2006. Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds, Oregon. J. Geophys. Res. 111, GO1007, doi:10.1029/2005JG000082.

House, W.A., Warwick, M.S., 1998. Hysteresis of the solute concentration/discharge relationship in rivers during storms. Water Res. 32, 2279-2290.

Howard, P.J., Cole, S.J., Robson, A.J., Moore, R.J., 2012. Raingauge quality-control algorithms and the potential benefits for radar-based hydrological modelling. In: Moore RJ, Cole SJ, Illingworth AJ editors. Weather Radar and Hydrology (Proc. Exeter Symp., April 2011) IAHS Publ. no. 351; 219-224.

Howarth, R.W., Billen, G., Swaney, D., Townsend, A., Jaworski, N., Lajtha, K. et al., 1996. Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: natural and human influences. Biogeochem. 35, 75–139.

Hur, J., Schlautman, M.A., 2004. Effects of pH and phosphate on the adsorptive fraction of purified Aldrich humic acid on kaolinite and hematite. J. Coll. Inter. Sci. 277, 264-270.

Imai, A., Fukushima, T., Matsushige, K., Kim, Y-H., Choi K., 2002. Characterization of dissolved organic matter in effluents from wastewater treatment plants. Water Res. 36, 859-870.

Jarvie, H.P., Neal, C., Withers, P.J.A., 2006. Sewage-effluent phosphorus: A greater risk to river eutrophication than agricultural phosphorus? Sci. Total Environ. 360, 246-253.

Johnes, P.J., Burt, T.P., 1993. Nitrate in surface waters T.P. Burt, A.L. Heathwaite, S.T. Trudgill (Eds.), Nitrate: processes, patterns and management, Wiley, Chichester, pp. 270–317.

Johnes, P.J., 1996.Evaluation and management of the impact of land use change on the nitrogen and phosphorus loads delivered to surface waters: the export coefficient modelling approach. J. Hydrol. 183, 323-349.

Jordan, E.T., Correll, D.L., Weller, D.E., 1997. Relating nutrient discharges from watersheds to land use and streamflow variability. Water Resour. Res. 33(11), 25779-2590.

Kim, L-H., Choi, E., Stenstrom, M.K., 2003. Sediment characteristics, phosphorus types and phosphorus release rates between river and lake sediments. Chemosphere 50, 53-61.

Lapworth, D.J., Gooddy, D.C., Allen, D., Old, G.H., 2009a. Understanding groundwater, surface water, and hyporheic zone biogeochemical processes in a Chalk catchment using fluorescence properties of dissolved and colloidal organic matter, J. Geophys. Res. 114, G00F02, doi:10.1029/2009JG000921.

Lapworth, D.J., Gooddy, D.G., Butcher, A., Morris, B., 2008 Tracing groundwater flow and sources of organic carbon in sandstone aquifers using fluorescence properties of dissolved organic matter (DOM), Applied Geochem. 23, 3384-3390.

Lapworth, D.J., Gooddy, D.G., Jarvie, H.P., 2011.Understanding phosphorus mobility and bioavailability in the hyporheic zone of a Chalk stream, J. Water Air and Soil Poll. 218, 213-226.

Lapworth, D.J., Kinniburgh, D.G., 2009b. An R Script for Visualising and Analysing Fluorescence Excitation–Emission Matrices (EEMs).Computers and Geoscience 30, 2160-2163.

Leenheer, J.A., Croue, J.P., 2003. Characterizing aquatic dissolved organic matter. Environ. Sci. Technol. 37, 18A-26A.

Li, X., Wang, Y., Stern, J., Gu, B., 2011. Isotope evidence for the source and fate of phosphorous in Everglades wetland ecosystems. Applied Geochem. 26(5), 688-695.

MAFF, 1993. Solving the nitrate problem: progress in research and development (PB 1092). MAFF publications, Admail 6000, London SW1A 2XX.

McKnight, D.M., Boyer, E.W., Westerhoff, P.K., Doran, P.T., Kulbe, T., Andersen, D.T., 2001. Spectrofluorometric characterisation of dissolved organic matter for indication of precursor organic material and aromaticity. Limnol. Oceanog. 46, 38–48.

McClain, M., Boyer, E.W., Dent, C.L., Regal, S.E., Grimm, N.B., Groffman, P.M. et al., 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. Ecosystems 6, 301-312.

Moore, R.J., Bell, V.A., Cole, S.J., Jones, D.A., 2007. Rainfall-runoff and other modelling for ungauged/low-benefit locations. Science Report – SC030227/SR1, Research Contractor: CEH Wallingford. Environment Agency, Bristol, UK, 249pp.

Moore, R.J., Cole, S.J., Bell, V.A., Jones, D.A., 2006. Issues in flood forecasting: ungauged basins, extreme floods and uncertainty. In: Frontiers in Flood Research (ed. by I. Tchiguirinskaia, K. N. N. Thein & P. Hubert), 8th Kovacs Colloquium, UNESCO, Paris, June/July 2006, IAHS Publ. 305, 103–122.

Moore, R.J., Jones, A.E., Jones, D.A., Black, K.B., Bell, V.A., 2004. Weather radar for flood forecasting: some UK experiences. 6th Int. Symp. on Hydrological Applications of Weather Radar, 2-4 February 2004, Melbourne, Australia, 11pp.

Morrison, M.A., Benoit, G., 2004. Investigation of conventional membrane and tangential flow ultrafiltration artifacts and their application to the characterization of freshwater colloids. Environ. Sci. Tech. 38, 6817-6823.

Merseburger, G.C., Eugènia, M., Sabater, F., 2005. Net changes in nutrient concentrations below a point source input in two streams draining catchments with contrasting land uses. Sci. Total Environ. 347, 217-229.

Meyer, J.L., Sale, M.J., Mulholland, P.J., Poff, N.L., 1999. Impacts of climate change on aquatic ecosystem functioning and health. J. Am. Water Res. Assoc. 35, 1373-1386.

Murphy, J., Riley, J.P., 1967. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27, 31-36.

Neal, C., Neal, M., Wickham, H., 2000. Phosphate measurements in natural waters: two examples of analytical problems associated with silica interference using phosphomolybdic acid methodologies. Sci. Total Environ. 251/252, 511-522.

Neal, C., Jarvie, H.P., Love, A., Neal, M., Wickham, H., Harman, S., 2008. Water quality along a river continuum subject to point and diffuse sources. J. Hydrol. 350, 156-165.

Neal, C., Jarvie, H.P., Withers, P.J.A., Whitton, B.A., Neal, M., 2010. The strategic significance of wastewater sources to pollutant phosphorus levels in English rivers and to environmental management for rural, agricultural and urban catchments. Sci. Total Environ. 408, 1485-1500.

Neal, C., Reynolds, B., Rowland, P., Norris, D., Kirchner, J.W., Neal, M., Sleep, D., Lawlor, A., Woods, C., Thacker, S., Guyatt, H., Vincent, C., Hockenhull, K., Wickham, H., Harman, S., Armstrong, L., 2012. High-frequency water quality time series in precipitation and streamflow: From fragmentary signals to scientific challenge. Sci Total Environ NRFA (National River Flow Archive). http://www.ceh.ac.uk/data/nrfa/index.html, last accessed on the 23rd March 2012.

Palmer-Felgate, E.J., Mortimer, R.J.G., Krom, M.D., Jarvie, H.P., 2010. Impact of point-source pollution on phosphorus and nitrogen cycling in stream-bed sediments. Environ. Sci. Tech. 44(3), 908-914.

Parlanti, E., Worz, K., Geoffroy, L., Lamotte, M., 2000. Dissolved organic matter spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs. Org. Geochem. 31, 1765-1781.

Price, D., Hudson, K., Boyce, G., Schellekens, J., Moore, R.J., Clark, P., Harrison, T., Connolly, E., Pilling, C., 2012. Operational use of a grid-based model for flood forecasting. Water Manage. 165(2), 65-77.

R Development Core Team, 2012. The R foundation for statistical computing, Vienna University of Technology, Vienna, Austria.

Schelske, C.L., Rothman, E.D., Stoermer, E.F., Santiago, M.A., 1974. Responses of phosphorus limited Lake Michigan phytoplankton to factorial enrichments with nitrogen and phosphorus. Limnol. Oceanogr. 19:409–419.

Schindler, D.W., 1974. Eutrophication and recovery in experimental lakes: Implications for lake management. Science 184:897–899.

Senesi, N., 1993. In: Organic substances in soil and water: natural constituents and their influences on contaminant behaviour; Bech, AJ, Jones, KC, Hayes, MBH, Mingelgrin, U, Eds.; The Royal Society of Chemistry: Cambridge p 74.

Stumm, W., 1977. Chemical interactions in particle separation. Environ. Sci. Tech. 11, 1066-1070.

Thurman, E.M., 1985. Organic geochemistry of natural waters. Martinus Nijhoff/Dr. W Junk Publishers, Boston.

Vane, C.H., Kim, A.W., McGowan, S., Leng, M.J., Heaton, T.H.E., Kendrick, C.P., Coombs, P., Yang, H., Swann, G.E.A., 2012. Sedimentary records of sewage pollution using faecal markers in contrasting peri-urban shallow lakes. Sci. Total Environ. 409, 345-356.

Wang, L., Stuart, M.E., Bloomfield, J.P., Butcher, A.S., Gooddy, D.C., McKenzie, A.A. et al., 2012. Prediction of the arrival of peak nitrate concentrations at the water table at a regional scale in Great Britain. Hydrol. Proc. 26, 226-239.

Wassenaar, L.I., 1995. Evaluation of the origin and fate of nitrate in the Abbortsford Aquifer using the isotopes of 15N and 18O in NO3-. Applied Geoch. 10, 391-405.

Water Framework Directive (WFD), Council of European Communities, 2000. Establishing a framework for community action in the field of water policy (WFD;2000/60/EC). Official Journal of EC L327, December.

Whitehead, P.G., Crossman, J., 2012. Macronutrient cycles and climate change: Key science areas and an international perspective. Sci. Total Environ. 434, 13-17.

Wilson, H.F., Xenopoulos, M.A., 2009. Effects of agricultural land use on the composition of fluvial dissolved organic matter. Nature Geo. 2, 37-41.

Withers, P.J.A., Jarvie, H.P., 2008. Delivery and cycling of phosphorus in rivers: A review. Sci. Total Environ. 400, 379-395.

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

Worssam, B.C., 1963. Geology of the country around Maidstone. Memoir of the British Geological Survey, Sheet 288, HMSO.

Worrall, F., Davies, H., Burt, T., Howden, N.J.K., Whelan, M.J., Bhogal, A., Lilly, A., 2012. The flux of dissolved nitrogen from the UK – Evaluating the role of soils and land use. Sci. Total Environ. 434,90-100.

Zolsay, A., Baigar, E., Jimenez, M., Stinweg, B., Saccomandi, F., 1999. Differentiating with fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying. Chemosphere 38, 45-50.

Table captions:

Table 1. Summary of the nutrient chemistry for the Beult catchment

Table 2. Summary ANOVA table for selected chemical variables

Table 3. TFF and fluorescence results

Figure captions:

Figure 1. Location of study area, sampling sites, drainage, geology and main population centres. a) Geology, drainage network and centres of population within the

Beult catchment; b)Location of the Beult catchment (shown in bold) as part of the Medway catchment, Kent, UK . Site numbers refer to sites in Table 1. * EA water level and flow monitoring sites. Population centres: a=Cranbrook, b=Smarden, c=Staplehurst, d=Headcorn, e=Stilebridge. Drainage data courtesy of CEH (NERC). Sites 4, 5 and 11 are located on a small low order tributary of the River Beult.

Figure 2. Long-term flow and nutrient data: a) Daily mean flow between 2003 and 2010 at Stilebridge, the outlet of the Beult catchment, b) NO_3-N, c) SRP-P, d) Molar N:P ratios. Red stars in Figure 2a show sampling rounds.

Figure 3. Ternary plot of DOC, SRP and NO_3. Circles show results during the storm flow survey, triangles results from the baseflow survey.

Figure 4. Phosphorus association with particulate, colloidal and dissolved fractions by TFF. a) storm flow results, b) baseflow results.

Figure 5. Nitrate N and O isotope results. a) Nitrate ^{15}N and ^{18}O cross plot, b) ^{15}N vs NO_3-N scatter plot. Filled symbols show results during storm flow conditions, open symbols show results during baseflow conditions. Numbers refer to sites, see Table 1. WW indicates sites that are impacted by wastewater sources, WWTW, discharge from wastewater treatment works.

Figure 6. G2G modelled flow at selected gauged and ungauged sites across the study area during the high-flow survey. River flows for the Beult at Romden Castle are provided for comparison. Catchment average rainfall and modelled soil moisture deficit are shown for the Romden Castle catchment area (top plots). The two main rainfall/runoff events during this period are highlighted and used in Figure 7 and 8.

Figure 7. Time-averaged G2G gridded runoff ratio and relationship to site nutrient flux during the storm flow survey a-b) DOC, c-d) NO_3-N, e-f) SRP. Left hand panels show results for the first storm event (21:00 08/11/08 – 01:00 09/11/08), and right hand panels for second event (07:00 10/11/08 – 01:00 11/11/08). Site numbers are shown in Figure 7a (see Table 1 for details).

Figure 8. Scatter plots of nutrient flux and catchment area. a) DOC, b) SRP, c) TDP, d) NO_3-N, e) DHP and f) Cl. Circle symbols are data from the first runoff event, square symbols are from the second runoff event. The red line shows a robust linear regression line for data from the first event.

Figure 1

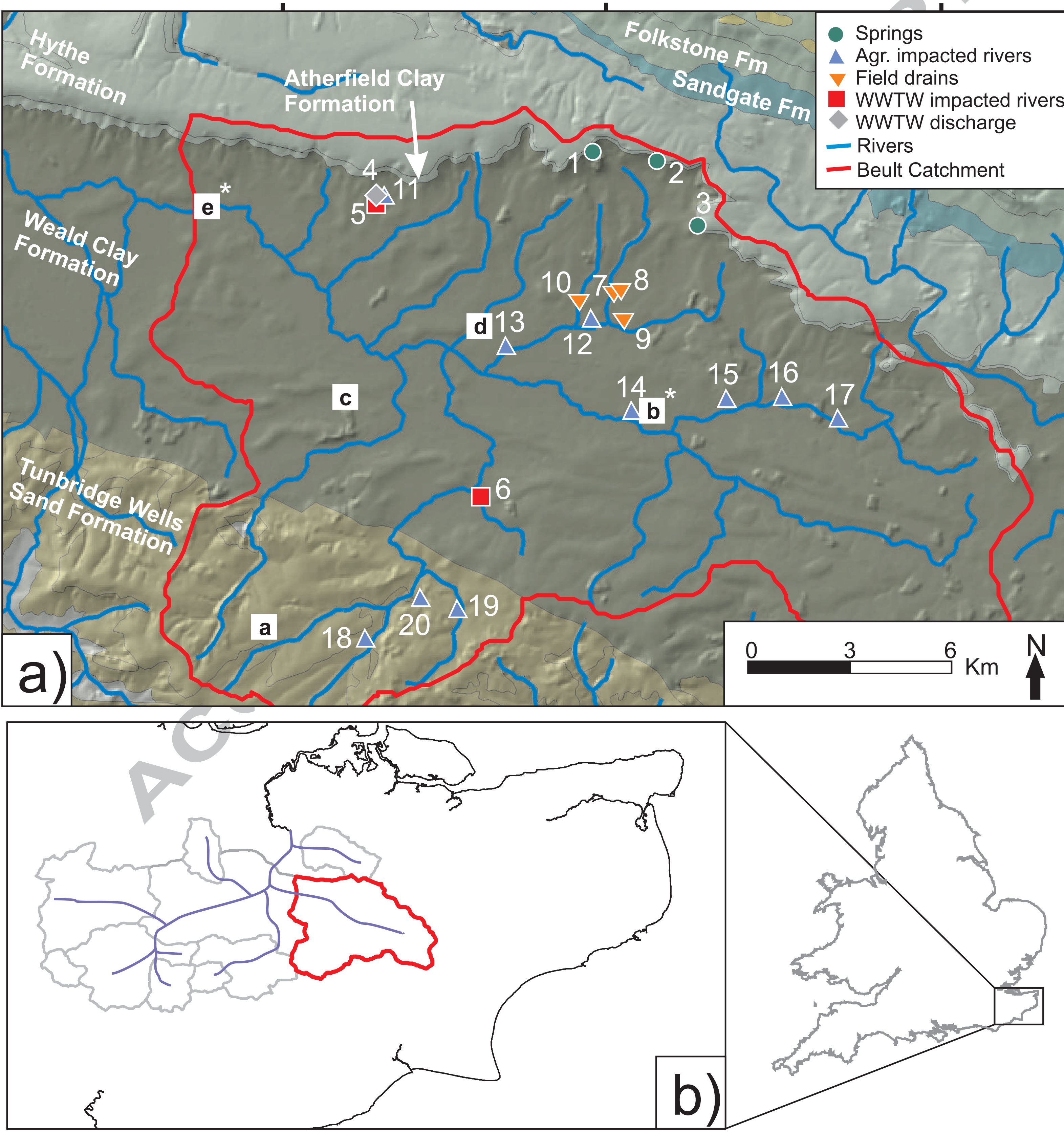
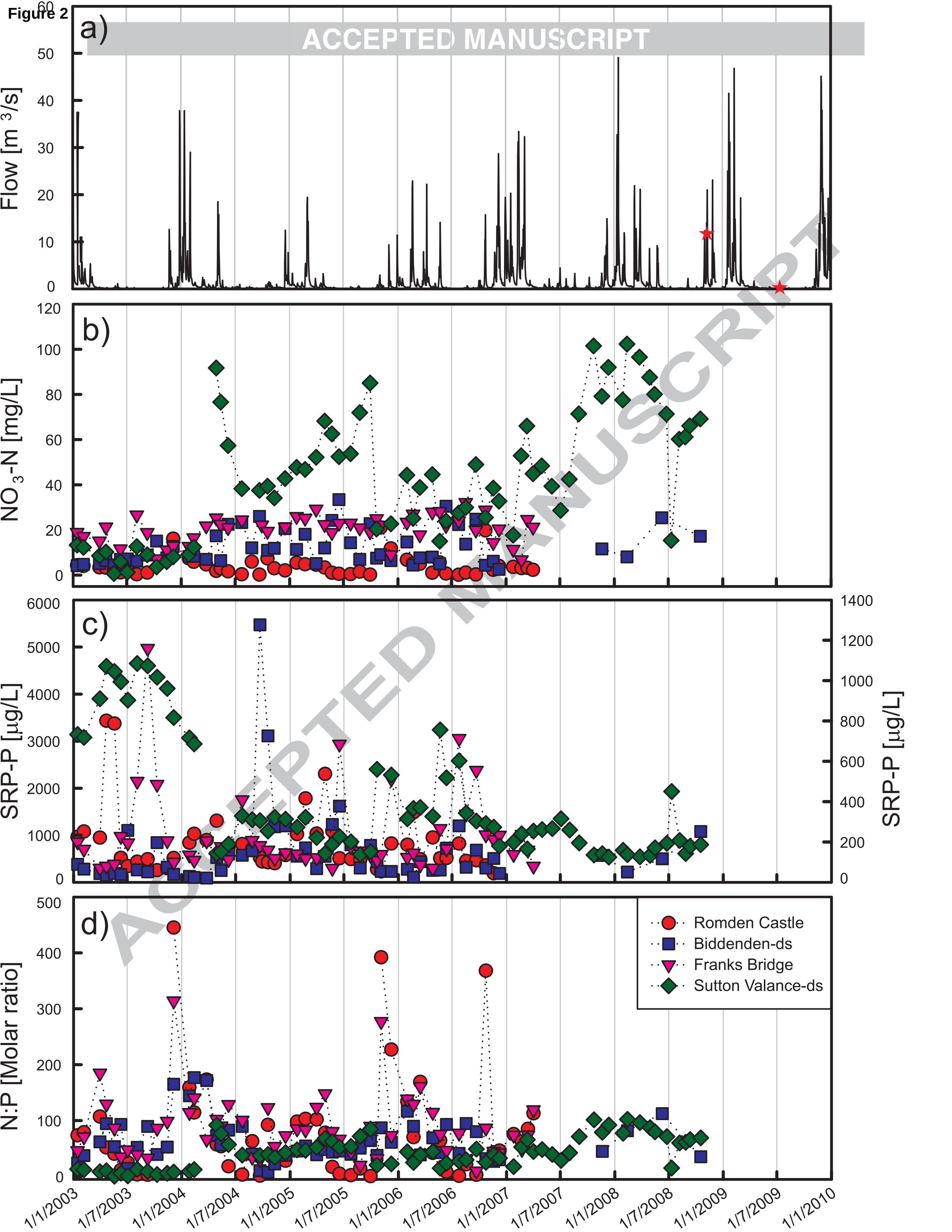

580000
588000
596000
145000
135000
Hythe Formation
Atherfield Clay Formation
Folkstone Fm
Sandgate Fm
Weald Clay Formation
Tunbridge Wells Sand Formation
Springs
Agr. impacted rivers
Field drains
WWTW impacted rivers
WWTW discharge
Rivers
Beult Catchment
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
a
b
c
d
e
0
3
6
Km
N
a)
b)

Figure 2



a)
Flow [m 3/s]
b)
NO3-N [mg/L]
c)
SRP-P [µg/L]
SRP-P [µg/L]
d)
N:P [Molar ratio]
Romden Castle
Biddenden-ds
Franks Bridge
Sutton Valance-ds
1/1/2003
1/7/2003
1/1/2004
1/7/2004
1/1/2005
1/7/2005
1/1/2006
1/7/2006
1/1/2007
1/7/2007
1/1/2008
1/7/2008
1/1/2009
1/7/2009
1/1/2010

Figure 3

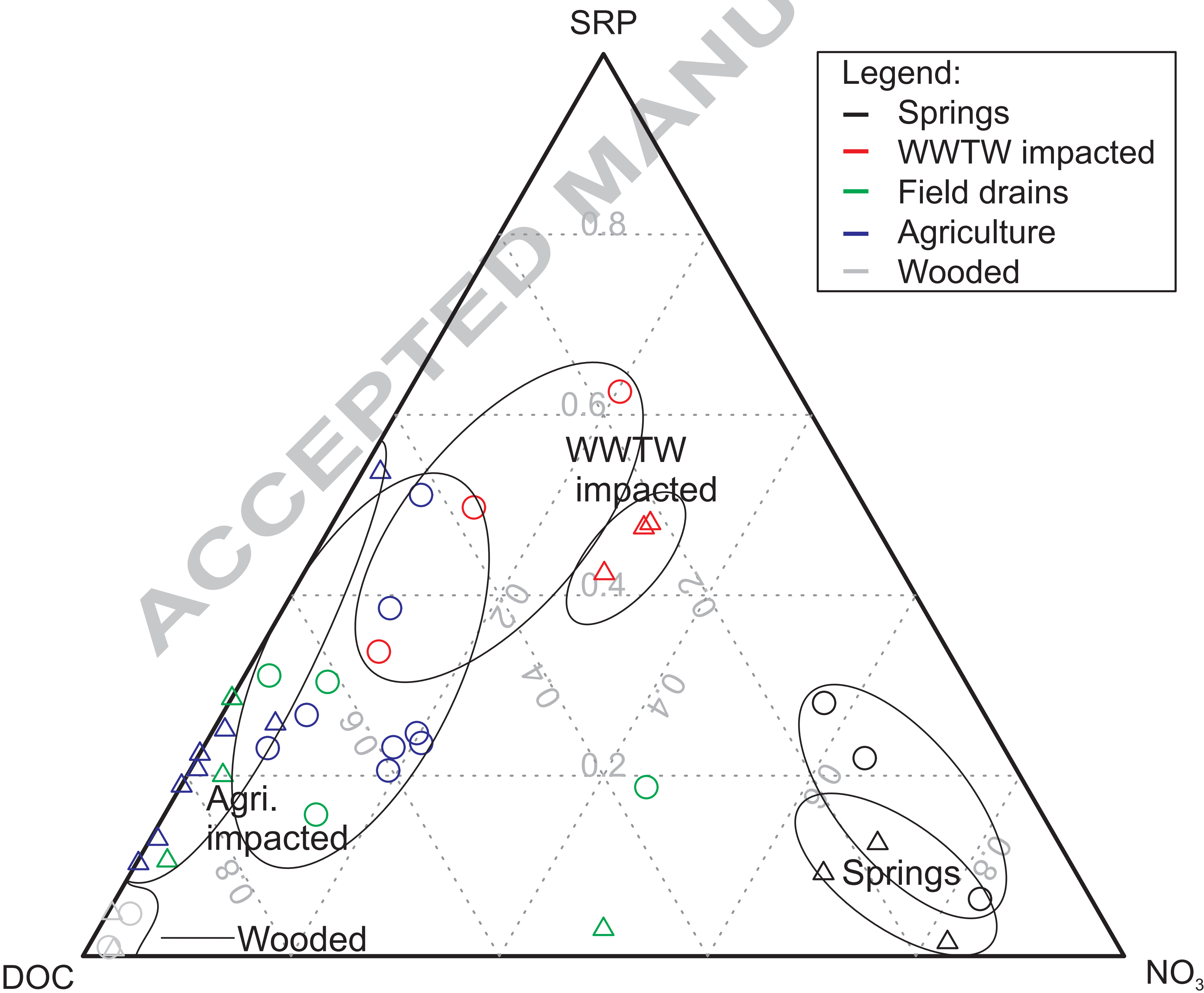
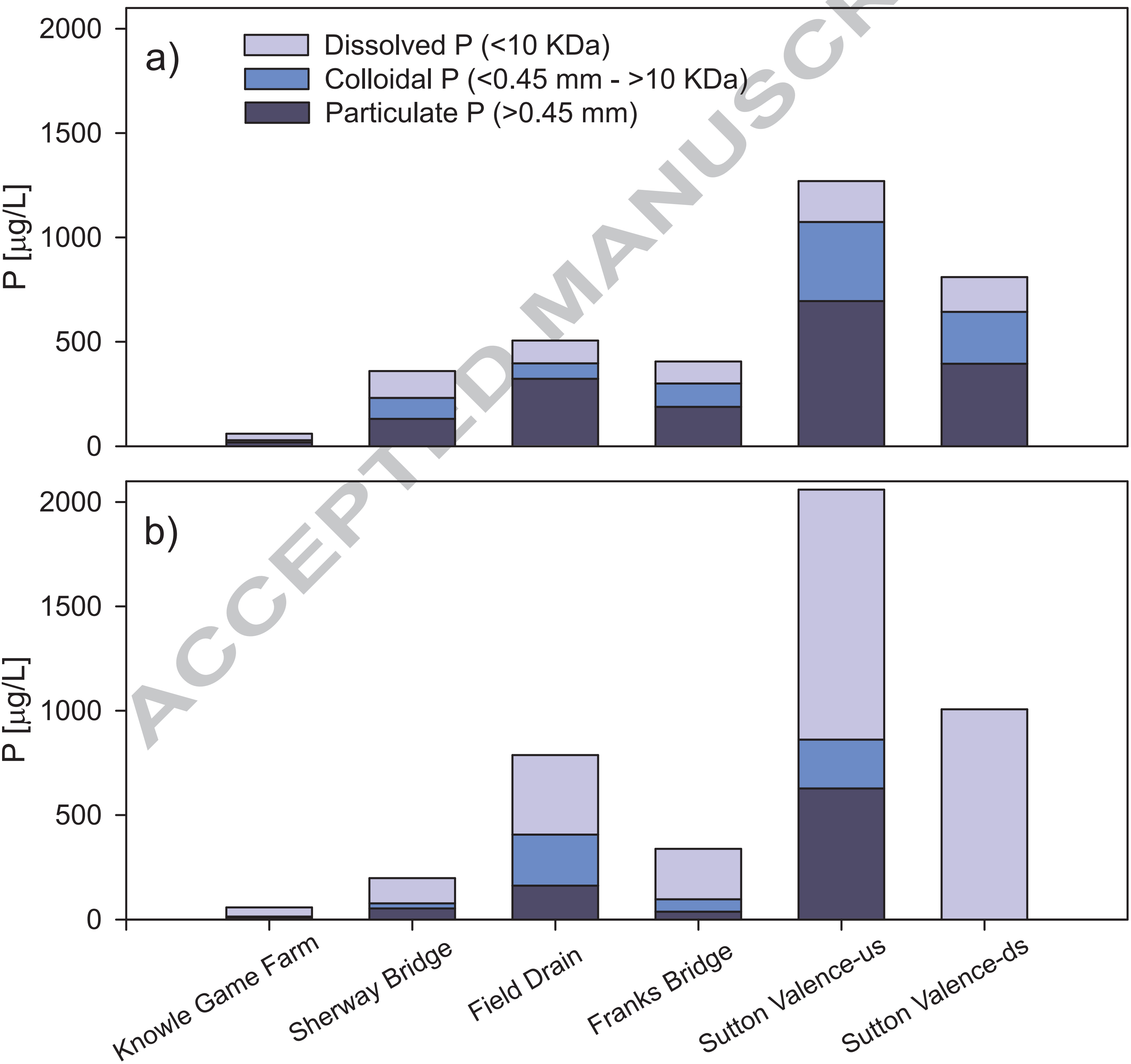

SRP
DOC
NO_3
Legend:
Springs
WWTW impacted
Field drains
Agriculture
Wooded
0.8
0.6
0.4
0.2
WWTW impacted
Agri. impacted
Springs
Wooded

Figure 4



a)
b)
Dissolved P (<10 KDa)
Colloidal P (<0.45 mm - >10 KDa)
Particulate P (>0.45 mm)
P [µg/L]
0
500
1000
1500
2000
Knowle Game Farm
Sherway Bridge
Field Drain
Franks Bridge
Sutton Valence-us
Sutton Valence-ds

Figure 5

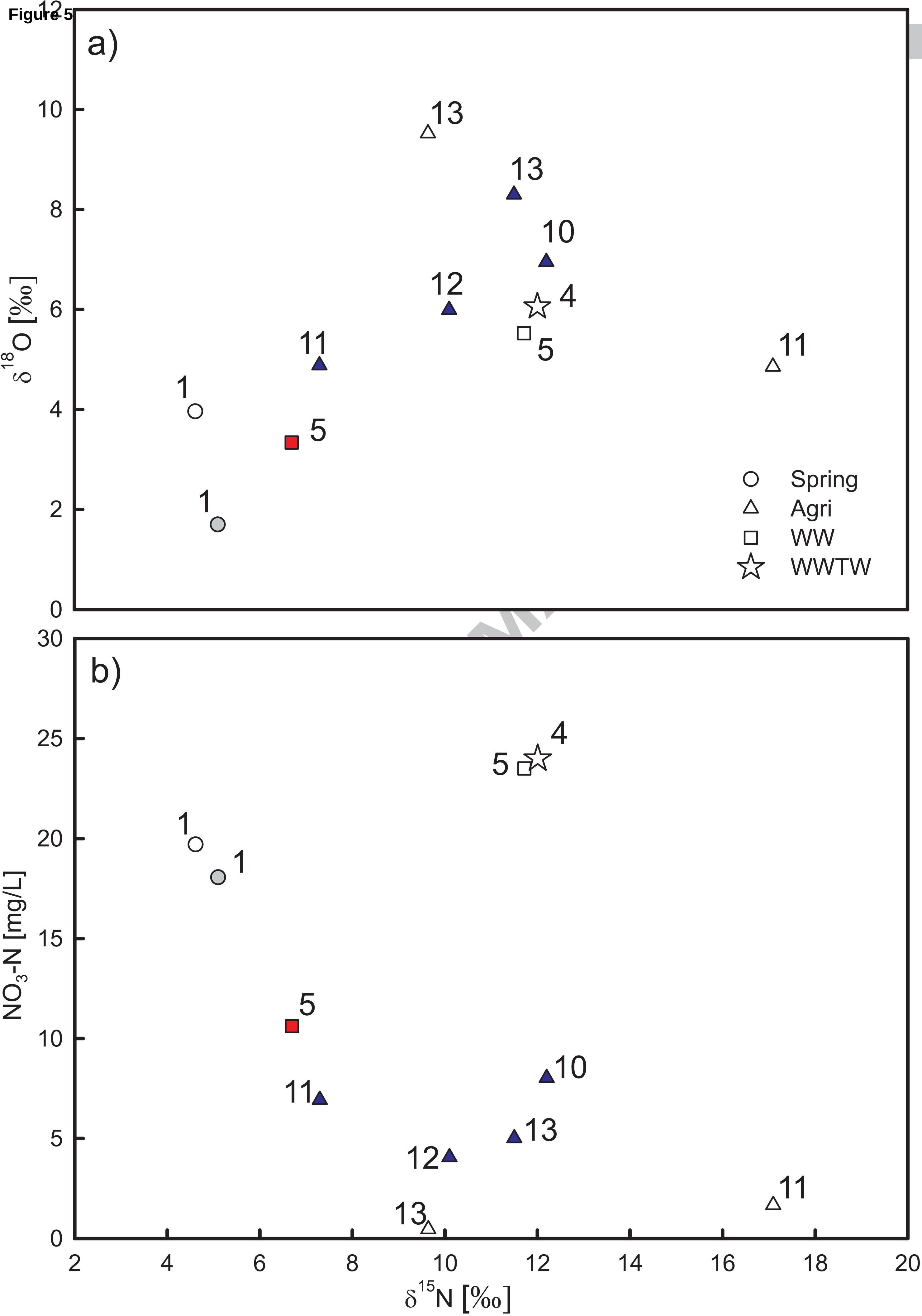
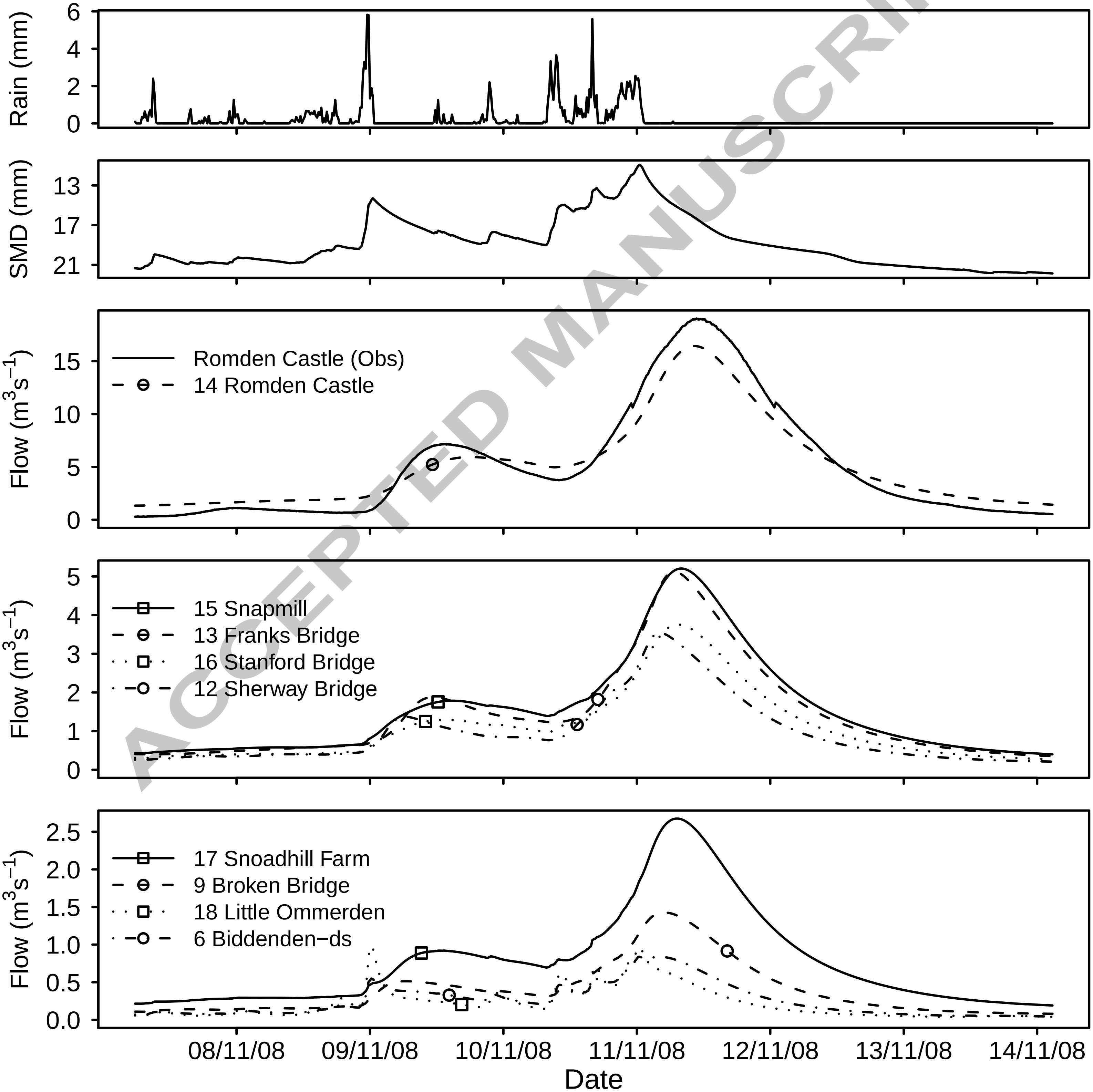
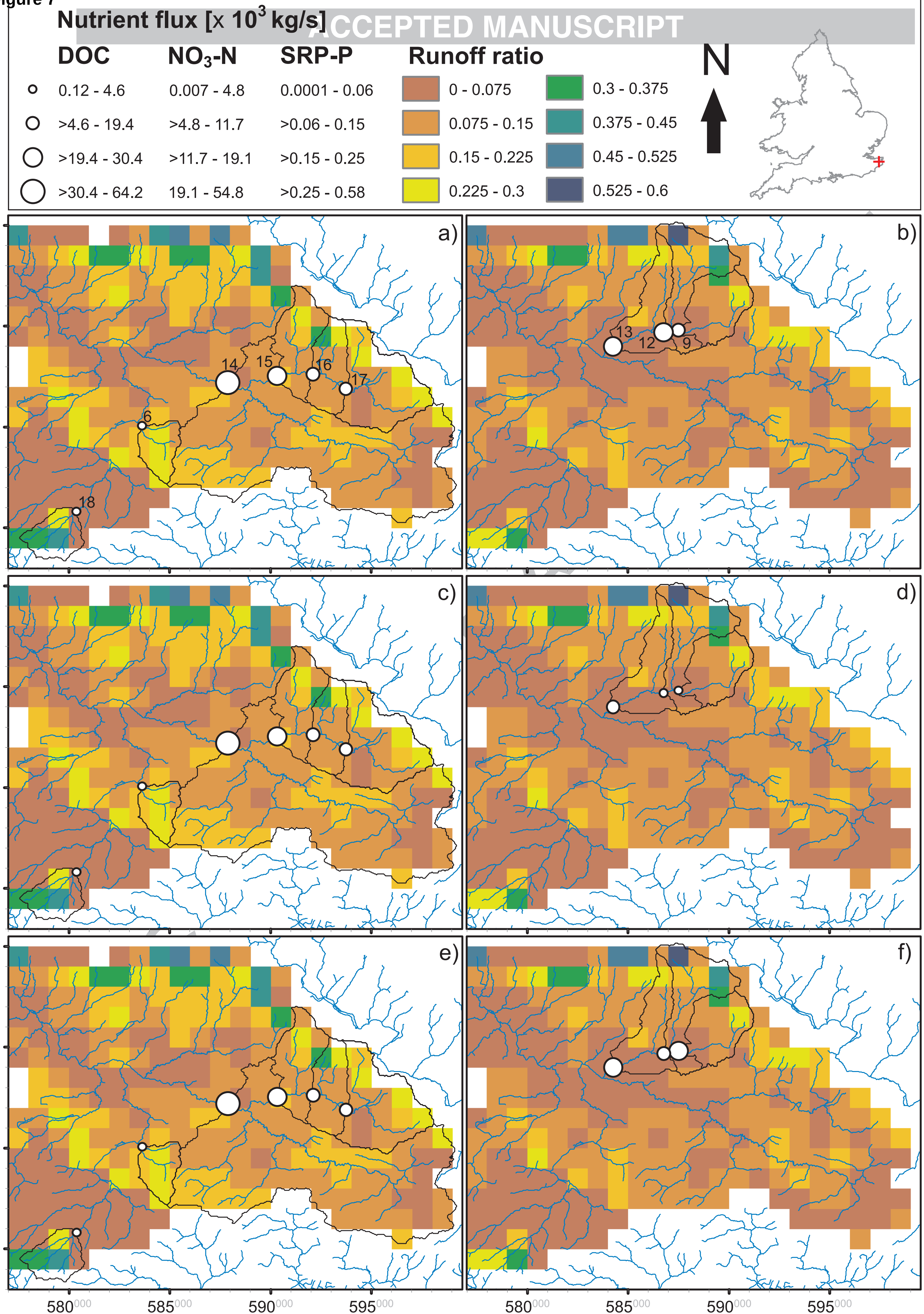


Figure 6



Rain (mm)
6
4
2
0
SMD (mm)
13
17
21
Flow (m^{3}s^{-1})
Romden Castle (Obs)
14 Romden Castle
15
10
5
0
15 Snapmill
13 Franks Bridge
16 Stanford Bridge
12 Sherway Bridge
17 Snoadhill Farm
9 Broken Bridge
18 Little Ommerden
6 Biddenden−ds
08/11/08
09/11/08
10/11/08
11/11/08
12/11/08
13/11/08
14/11/08
Date

Figure 7



Nutrient flux [x 10^3 kg/s]
DOC
NO3-N
SRP-P
Runoff ratio
0.12 - 4.6
>4.6 - 19.4
>19.4 - 30.4
>30.4 - 64.2
0.007 - 4.8
>4.8 - 11.7
>11.7 - 19.1
19.1 - 54.8
0.0001 - 0.06
>0.06 - 0.15
>0.15 - 0.25
>0.25 - 0.58
0 - 0.075
0.075 - 0.15
0.15 - 0.225
0.225 - 0.3
0.3 - 0.375
0.375 - 0.45
0.45 - 0.525
0.525 - 0.6
N
a)
b)
c)
d)
e)
f)
14
15
16
17
6
18
13
12
9
150000
145000
140000
135000
580000
585000
590000
595000

Figure 8

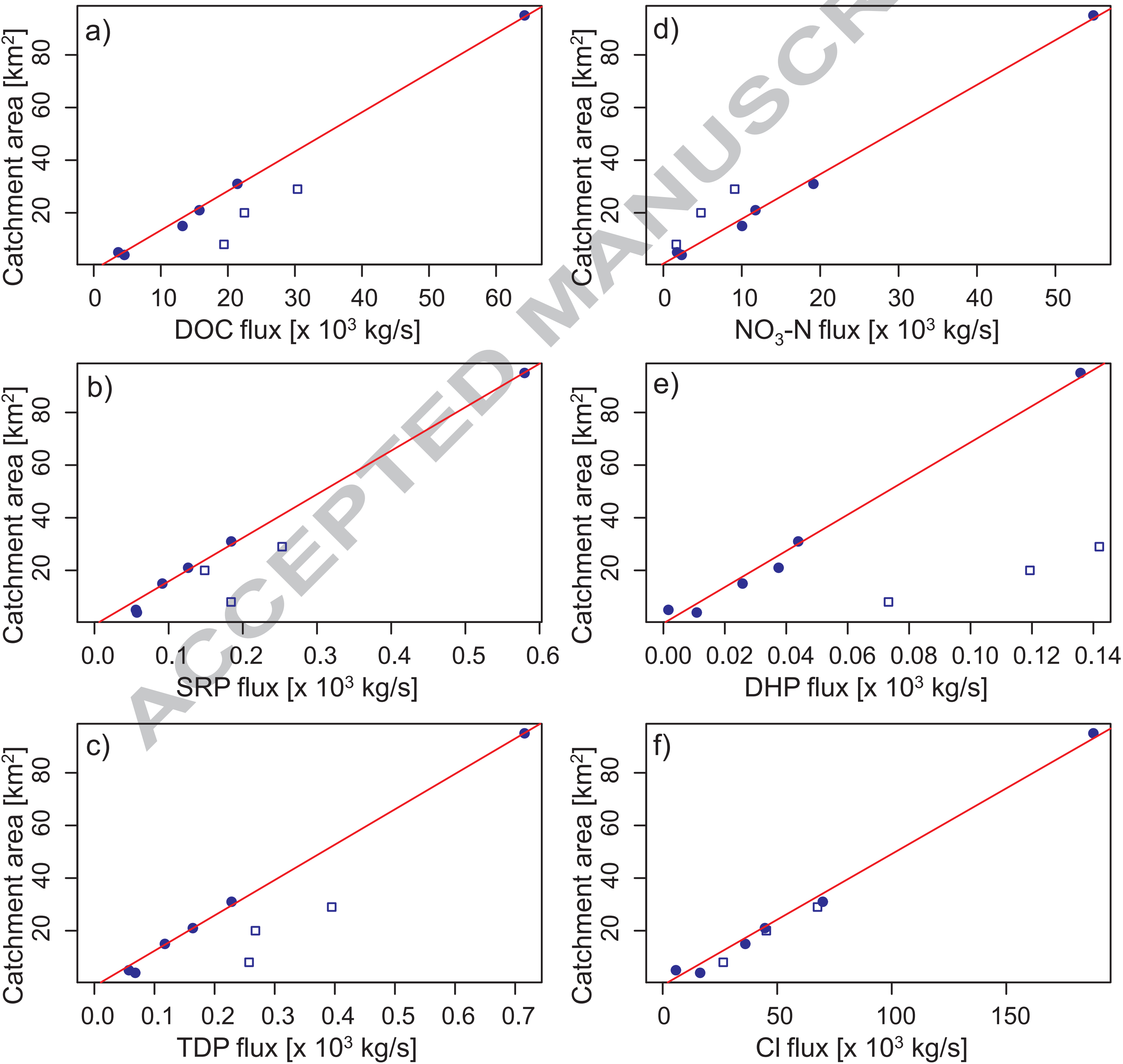

a)
Catchment area [km²]
DOC flux [x 10³ kg/s]
d)
Catchment area [km²]
NO3-N flux [x 10³ kg/s]
b)
Catchment area [km²]
SRP flux [x 10³ kg/s]
e)
Catchment area [km²]
DHP flux [x 10³ kg/s]
c)
Catchment area [km²]
TDP flux [x 10³ kg/s]
f)
Catchment area [km²]
Cl flux [x 10³ kg/s]
ACCEPTED MANUSCRIPT

Table1-3

Table 1.

Variable	DOC	DOC	NO_3-N	NO_3-N	TDP	TDP	SRP	SRP	DHP	DHP	TP	TP	PP	PP	N:P	N:P	SRP:DHP	SRP:DHP	SRP	SRP	DHP	DHP
Unit	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L					%	%	%	%
Sampling round	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2
Springs																						
1 Knowle Game Farm	1.1	1.0	20.2	19.7	42	31	13	9	29	22	60	45	18	14	3437	4853	0.4	0.4	31	29	69	71
2 Hollis Farm	1.2	1.3	13.2	13.3	41	48	38	45	<7	3	47	N/A	<7	N/A	766	654	12.7	15.0	93	94	7	6
3 Pope Hall	1.5	0.8	13.8	12.5	84	56	57	55	27	1	85	N/A	<7	N/A	534	505	2.1	55.0	68	98	32	2
Mean	1.3	1.0	15.7	15.2	56	45	36	36	28	8.7	64	45	18	14	1579	2004	1.8	2.8	64	74	36	26
WWTW discharge																						
4 Sutton Valence	3.5	4.4	10.0	24.0	266	1004	260	928	<7	76	276	992	10	<7	85	57	43.3	12.2	98	92	2	8
WWTW impacted rivers																						
5 Sutton Valence-ds	13.0	4.5	10.6	23.5	415	1000	349	912	66	92	810	1006	395	<7	67	57	5.3	10.4	84	91	16	9
6 Biddenden-ds	13.9	9.1	7.1	35.1	207	1344	174	1268	33	76	330	N/A	123	N/A	90	61	5.3	16.7	84	94	16	6
Mean	13.5	6.8	8.8	29.3	311	1172	262	1090	49.5	84	570	1006	259	<7	78	59	5.3	12.8	84	93	16	7
Field drains																						
7 Southernden	16.4	4.7	5.3	0.8	247	144	165	117	82	27	424	N/A	177	N/A	72	15	2.0	4.3	67	81	33	19
8 Little Southernden	17.3	13.4	51.0	51.6	242	101	180	78	62	23	426	170	184	69	627	1463	2.9	3.4	74	77	26	23
9 Broken Bridge	21.2	7.7	1.8	1.0	281	142	201	89	80	53	436	N/A	155	N/A	20	24	2.5	1.7	72	63	28	37
10 Field Drain	16.0	14	8.0	0.03	183	626	73	530	110	96	506	788	323	162	243	0.1	0.7	5.5	40	85	60	15
Mean	17.7	10	16.5	13.4	238	253	155	203.5	83.5	50	448	479	210	116	240	376	1.7	3.2	63	76	37	24
*Agriculturally impacted rivers**																						
11 Sutton Valence-us	17.4	11.0	6.9	1.7	575	1432	430	1252	145	180	1270	2060	695	628	35	3	3.0	7.0	75	87	25	13
12 Sherway Bridge	19.2	7.5	4.1	0.2	229	145	127	106	102	39	360	198	131	53	71	5	1.2	2.7	55	73	45	27
13 Franks Bridge	16.7	8.0	5.0	0.5	217	301	139	256	78	45	406	339	189	38	80	4	1.8	5.7	64	85	36	15
14 Romden Castle	12.3	10.4	10.5	0.3	137	297	111	259	26	38	698	N/A	561	N/A	209	3	4.3	6.8	81	87	19	13
15Snapmill	12.2	11.6	10.9	0.1	130	320	105	126	25	194	867	N/A	737	N/A	230	2	4.2	0.6	81	39	19	61
16 Stanford Bridge	12.6	12.4	9.4	0.02	131	499	101	339	30	160	570	N/A	439	N/A	207	0.2	3.4	2.1	77	68	23	32
17 Snoadhill Farm	14.9	15.8	11.3	0.04	132	404	103	348	29	56	510	N/A	378	N/A	243	0.2	3.6	6.2	78	86	22	14
18 Little Ommerden	18.0	8.7	8.6	2.8	283	342	275	310	8	32	429	N/A	146	N/A	70	20	34.4	9.7	97	91	3	9
Mean	15.4	10.7	8.3	0.7	229	468	174	375	55	93	639	866	410	240	143	5	3.2	3.4	76	77	24	23
Wooded catchment																						
19 Rogley Hill	11.7	4.9	0.7	0.1	34	32	12	23	22	9	218	N/A	184	N/A	122	8	0.5	2.6	35	72	65	28
20 Chittenden wood	17.0	4.9	0.8	0.5	10	10	<7	3.5	<7	6.5	24	N/A	14	N/A	533	323	0.5	0.5	35	35	65	65
Mean	14.4	4.9	0.8	0.3	22	21	12	13.25	22	7.75	121	N/A	99	N/A	327	165	0.5	1.1	35	53	65	47

R1=High flow conditions, R2=Baseflow conditions, *predominantly agricultural with limited WW inputs, N:P are NO3:SRP (molar ratios).

Table 1 continued

Variable	NO_3-N :Cl	NO_3-N :Cl	TDP:Cl	TDP:Cl	SRP:Cl	SRP:Cl
Sampling round	R1	R2	R1	R2	R1	R2
Springs						
1 Knowle Game Farm	0.834	0.851	0.002	0.001	0.001	0.000
2 Hollis Farm	0.400	0.439	0.001	0.002	0.001	0.001
3 Pope Hall	0.508	0.445	0.003	0.002	0.002	0.002
Mean	0.560	0.558	0.002	0.002	0.001	0.001
WWTW discharge						
4 Sutton Valence	NA	0.270	NA	0.011	NA	0.010
WWTW impacted rivers						
5 Sutton Valence-ds	0.214	0.266	0.008	0.011	0.007	0.010
6 Biddenden-ds	0.142	0.280	0.004	0.011	0.004	0.010
Mean	0.178	0.274	0.006	0.011	0.005	0.010
Field drains						
7 Southernden	0.183	0.024	0.008	0.004	0.006	0.003
8 Little Southernden	1.747	1.088	0.008	0.002	0.006	0.002
9 Broken Bridge	0.062	0.016	0.010	0.002	0.007	0.002
10 Field Drain	0.206	0.001	0.005	0.018	0.002	0.016
Mean	0.524	0.307	0.008	0.006	0.005	0.005
*Agriculturally impacted rivers**						
11 Sutton Valence-us	0.153	0.032	0.013	0.027	0.010	0.024
12 Sherway Bridge	0.105	0.005	0.006	0.003	0.003	0.002
13 Franks Bridge	0.135	0.011	0.006	0.007	0.004	0.006
14 Romden Castle	0.292	0.005	0.004	0.004	0.003	0.004
15 Snapmill	0.274	0.001	0.003	0.005	0.003	0.002
16 Stanford Bridge	0.264	0.000	0.004	0.005	0.003	0.004
17 Snoadhill Farm	0.278	0.001	0.003	0.007	0.003	0.006
18 Little Ommerden	0.304	0.020	0.010	0.002	0.010	0.002
Mean	0.222	0.010	0.006	0.007	0.005	0.005
Wooded catchment						
19 Rogley Hill	0.022	0.002	0.001	0.001	0.000	0.000
20 Chittenden wood	0.022	0.012	0.000	0.000	NA	0.000
Mean	0.022	0.006	0.001	0.000	0.000	0.000

Table 2.

Variable	Source[a]	Round[b]
pH	0.00084 ***	0.01088 *
SEC	1.0e-11 ***	3.7e-09 ***
HCO_3	3.3e-06 ***	1.8e-05 ***
SO_4	9.9e-05 ***	0.52
Cl	2.6e-06 ***	2.0e-05 ***
DOC	3.4e-15 ***	6.4e-05 ***
NO_3	0.0011 **	0.0013 **
TDP	0.00067 ***	0.01225 *
SRP	0.00046 ***	0.00951 **
DHP	0.029 *	0.361
NO3:SRP	0.00056 ***	0.00044 ***

[a]Grouped according to source type (see Table 1).

[b]Grouped by sampling occasions R1 and R2

Significance denoted as follow: 0 *** 0.001 **0.01 * 0.05

Table 3.

Variable	DP	DP	FA	FA	TRP	TRP	TY	TY	FI	FI	β/α	β/α	HI	HI	TRP:FA	TRP:FA
Unit	μg/L	μg/L	R.U	R.U	R.U	R.U	R.U	R.U								
Sampling round	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2
1. Knowle Game Farm	31	44	0.1	0.1	0.18	0.20	0.09	0.26	1.59	1.62	0.68	0.71	1.55	1.48	1.77	1.66
5. Sutton Valence-ds	166	1004	12.6	1.7	3.33	0.66	0.99	0.25	1.60	1.60	0.57	0.79	17.62	8.96	0.26	0.38
10. Field Drain	109	381	15.9	3.3	3.31	0.95	0.98	0.31	1.45	1.53	0.56	0.53	21.08	15.67	0.21	0.29
11. Sutton Valence-us	196	1198	10.4	2.7	2.45	0.90	0.80	0.25	1.54	1.61	0.59	0.64	19.16	12.74	0.24	0.34
12. Sherway Bridge	129	121	17.0	1.6	3.54	0.48	0.85	0.25	1.60	1.51	0.57	0.59	20.02	11.46	0.21	0.31
13. Franks Bridge	105	242	15.8	1.7	3.33	0.59	0.82	0.26	1.54	1.70	0.56	0.57	21.21	12.24	0.21	0.34

DP = 'truly' dissolved P (<10 Kda), RU= Raman Unit, fluorescence indices (see section 3.3.3 for full explanations): FA=Fulvic acid, TRP=Tryptophan,

TY=Tyrosine, FI=fluorescence index (McKnight et al., 2001), β/α=labile/recalcitrant OM ratio (Parlanti et al., 200), HI=humification index (Zsolnay et al., 2001).

Multi technique approach to understand C, N and P within catchment processes

Changes in nutrient stoichiometry/bioavailability under contrasting flow conditions

N and O isotopes show dominance of waste water (WW) inputs during baseflow

Fluorescence DOM indices characterise WW inputs to rivers

Grid-to-Grid distributed model used to assess spatial variations in nutrient flux