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Hydrochemical processes in lowland rivers: insights from in situ, high-resolution monitoring

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Abstract. This paper introduces new insights into the hydrochemical functioning of lowland river systems using field-based spectrophotometric and electrode technologies. The streamwater concentrations of nitrogen species and phosphorus fractions were measured at hourly intervals on a continuous basis at two contrasting sites on tributaries of the River Thames – one draining a rural catchment, the River Enborne, and one draining a more urban system, The Cut. The measurements complement those from an existing network of multi-parameter water quality sondes maintained across the Thames catchment and weekly monitoring based on grab samples. The results of the sub-daily monitoring show that streamwater phosphorus concentrations display highly complex dynamics under storm conditions dependent on the antecedent catchment wetness, and that diurnal phosphorus and nitrogen cycles occur under low flow conditions. The diurnal patterns highlight the dominance of sewage inputs in controlling the streamwater phosphorus and nitrogen concentrations at low flows, even at a distance of 7 km from the nearest sewage treatment works in the rural River Enborne. The time of sample collection is important when judging water quality against ecological thresholds or standards. An exhaustion of the supply of phosphorus from diffuse and multiple septic tank sources during storm events was evident and load estimation was not improved by sub-daily monitoring beyond that achieved by daily sampling because of the eventual reduction in the phosphorus mass entering the stream during

events. The results highlight the utility of sub-daily water quality measurements and the discussion considers the practicalities and challenges of in situ, sub-daily monitoring.

1 Introduction

The chemical and ecological status of surface waters is an increasing concern worldwide as demand for water and food grows with population increases. River system water quality is affected by changes in the controlling factors of land use and management, atmospheric deposition, water usage and climate; much research has been devoted to the development of integrated catchment management strategies to protect and improve the freshwater resource and ecological status whilst the landscape is used for homes, industry, farming, forestry and recreation (Beman et al., 2005; Boyer et al., 2006). The spatial and temporal variations in streamwater chemistry are highly complex and the links between these changes and the controlling factors are subject to intense study, yet the interactions between the physical and chemical environment of rivers and their ecological status are poorly understood (Hilton et al., 2006). More work is required to improve understanding of the hydrochemical changes at sub-daily intervals to elucidate the links between the physical and chemical environment of a river system and its ecological structure, function and biodiversity (Elsenbeer et al., 1994; Bowes et

al., 2009a; Neal et al., 2012a). In particular, work is needed to determine if chemical thresholds have meaning when assessing ecological status to implement the European Union Water Framework Directive (WFD) and Habitats Directive.

The development of new methods of high-frequency water quality measurement has been identified as likely to lead to conceptual and practical advances in the hydrological and biogeochemical sciences since the critical need for sub-daily measurements of water quality has been established, not only for the nutrients, but also for many other chemicals (Neal et al., 2012b). Monitoring catchment hydrochemistry for long periods of time under diverse hydrologic regimes maximises the chances for serendipitous discoveries and improves the characterisation of pollutant sources and pathways, especially during storm events (Kirchner et al., 2000, 2004). There has long been a mismatch between measurement of water fluxes over gauging structures, which are often sub-hourly, and the measurement of most nutrient fluxes, which are usually daily at best and more often weekly or monthly. Continuous pH, water temperature, dissolved oxygen, turbidity, conductivity and chlorophyll *a* measurements have been available since the 1990s and these suggest that high-frequency chemical analysis of these, and other analytes, will lead to deeper insights into the contribution of chemicals to the river network via different flow pathways (Robson et al., 1995; Jarvie et al., 2001, 2003). Intensive (sub-daily) discrete sampling programmes have been employed by some researchers, such as Scholefield et al. (2005) in Devon, south-west England and Neal et al. (2012b) in Plynlimon, mid-Wales, to collect high-frequency hydrochemical data. These data have demonstrated complex diurnal patterns and provided new insights into the temporal variability of nutrient fluctuations. Such intensive manual sampling programmes are, however, impractical to sustain for prolonged periods, both in terms of physical and financial resources, and because samples, returned to the laboratory for analysis, are also subject to issues of sample stability (Halliday et al., 2012). Automated instrumental methods are needed to make progress by minimising sample degradation and allowing the study of short-term dynamics when the instream biological response is likely to be most evident (Horsburgh et al., 2010).

Recent developments in field-based analytical systems are now producing the first long-term, continuous, in situ measurements of some nutrients in water (Jordan et al., 2005; Palmer-Felgate et al., 2008; Soulsby et al., 2009) and enhancing previous studies that measured storm runoff quality in upland and lowland settings (Davies et al., 1992; Evans and Tranter, 1998; Deletic and Maksimovic, 1998). The data generated from in situ studies have been used to demonstrate the benefits of high-frequency sampling in areas such as load estimation accuracy (Rozemeijer et al., 2010; Jordan and Cassidy, 2011; Ferrant et al., 2012). There are also practical applications in that industrial discharge consents are often based on load estimates, and high-frequency monitoring provides real-time warning of pollution events and will likely

ultimately lead to altered modelling paradigms (e.g. Scher et al., 2002; Feng et al., 2004; Kirchner et al., 2004). To date, the deployment of in situ analytical equipment in the field for the purpose of assessing streamwater phosphorus (P) and nitrogen (N) concentrations has been reported in a growing number of studies (Jordan et al., 2005, 2007, 2012; Scholefield et al., 2005; Palmer-Felgate et al., 2008; Rozenmeijer et al., 2010; Fealy et al., 2010; Wall et al., 2011; Melland et al., 2012; Mellander et al., 2012a,b). These studies have tended to focus on specific nutrients, such as N (mainly as nitrate, NO₃) or P, in rural catchments. In addition, little detail exists on the challenges faced with regard to the field deployment of these devices.

The aim of the work presented here is to describe new insights into the hydrochemical functioning of larger lowland rural and urban river systems based on an analysis of new high-frequency data derived from field-based spectrophotometric equipment similar in scope to that reported elsewhere (e.g. Wall et al., 2011). Two river monitoring sites in the Thames catchment were established to operate alongside a larger network of electrode water quality sensors deployed and maintained by the England and Wales Environment Agency (EA). Of the two sites, the River Enborne at Brimpton is a rural river catchment draining Tertiary clay and The Cut at Bray is a drainage channel dominated by urban runoff and treated sewage effluent. In addition to insights into the water quality dynamics of these sites and ecosystem function in The Cut in terms of a preliminary analysis of productivity, photosynthesis and respiration, this paper also considers the challenges associated with running analytical instrumentation in the field and details the methodologies.

2 Study areas

Three monitoring sites were established in the catchment of the River Thames (9948 km² measured to the tidal limit at Kingston upon Thames) as part of the LIMPIDS project. The River Thames is a major river system in southern and eastern England (Fig. 1). The three sites were the River Enborne at Brimpton, the River Kennet at Clatford and The Cut at Bray. Of these sites, high-frequency water quality datasets were obtained for the River Enborne and The Cut. The high-frequency monitoring of the water quality in the River Kennet proved too difficult because the site did not have mains electricity, but the site and monitoring installation are described as they are both referred to in this article.

The surface water and groundwater of the Thames are an important regional resource providing water for most of the 20 million people that live within the catchment. The quality of these water resources is impacted by nutrient inputs from sewage and industrial effluent and runoff from farms and farmland (Neal et al., 2010). The EA have deployed and maintain and operate a sensor web network across the Thames catchment with 46 sites instrumented. Hourly

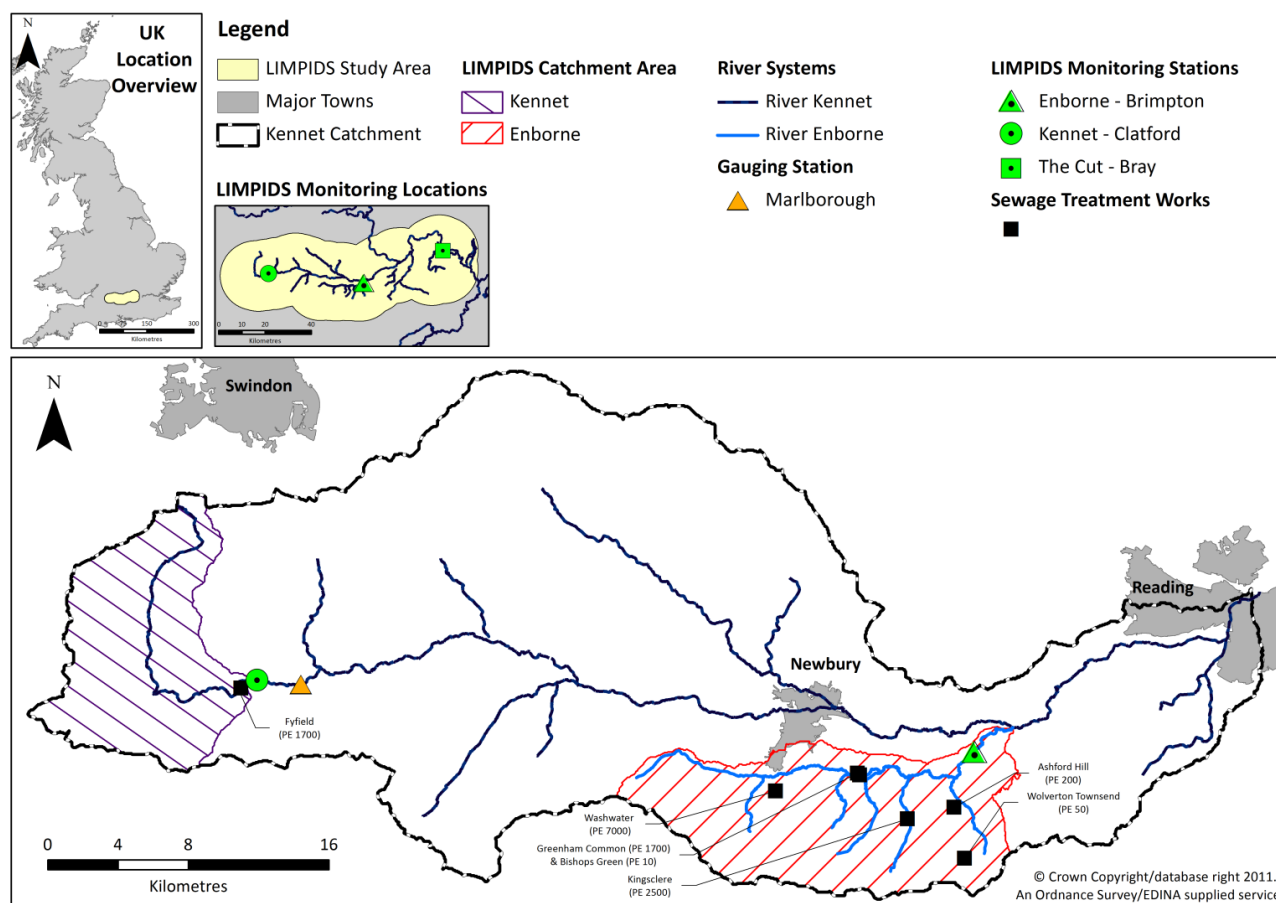


Fig. 1. The River Kennet and River Enborne study areas.

measurements are made with existing multi-parameter water quality sondes (YSI Inc., Ohio, USA) that are connected to a Meteor Communications telemetry system that transmits the measurement data, in real-time, to a central database.

2.1 The River Enborne at Brimpton

The River Enborne drains an area of approximately 148 km² and is a tributary of the River Kennet (Fig. 1). The Enborne catchment is predominantly rural and underlain by Cretaceous Chalk in the headwaters and Tertiary clays in the lower reaches. The base flow index is 0.53 and this is indicative of the greater importance of surface and near-surface hydrological pathways due to the impervious clays. The value of the index for the River Enborne is lower than nearby Cretaceous Chalk-dominated catchments, such as the upper Kennet, for which the base flow index is approximately 0.95. There are two sewage treatment works (STW) on the Enborne: Greenham, population equivalent (PE) 1700, and Bishop's Green, PE 10. Both are located approximately 7 km upstream of the flow gauging station and water quality monitoring site at Brimpton (Fig. 1). Further works are also located at Washwater on the Pound Street Brook (PE 7000) and at Kingsclere

on the Kingsclere Brook (PE 2500), and there are two minor works at Wolverton Townsend (PE 50) and Ashford Hill (PE 200) on the Baughurst Brook. All enter the River Enborne upstream of the Brimpton monitoring site (Fig. 1). The sediment and phosphorus dynamics of the River Enborne is thought to be controlled by diffuse inputs with subsequent instream processing (Evans and Johnes, 2004; Evans et al., 2004). The relief of the Enborne catchment is characterised by gently sloping valleys with a maximum altitude of 296 m a.s.l. The long-term annual precipitation over the catchment is 790 mm, though only approximately 50 % becomes river flow due to high evapotranspiration and groundwater storage (Marsh and Hannaford, 2008). The catchment provides water for public and industrial supply by means of groundwater abstractions.

2.2 The River Kennet at Clatford

The River Kennet drains an area of approximately 1200 km² and is a major tributary of the River Thames (Fig. 1). The River Kennet flows broadly eastwards for approximately 40 km before entering the River Thames at Reading. Cretaceous Chalk covers approximately 80 % of the catchment.

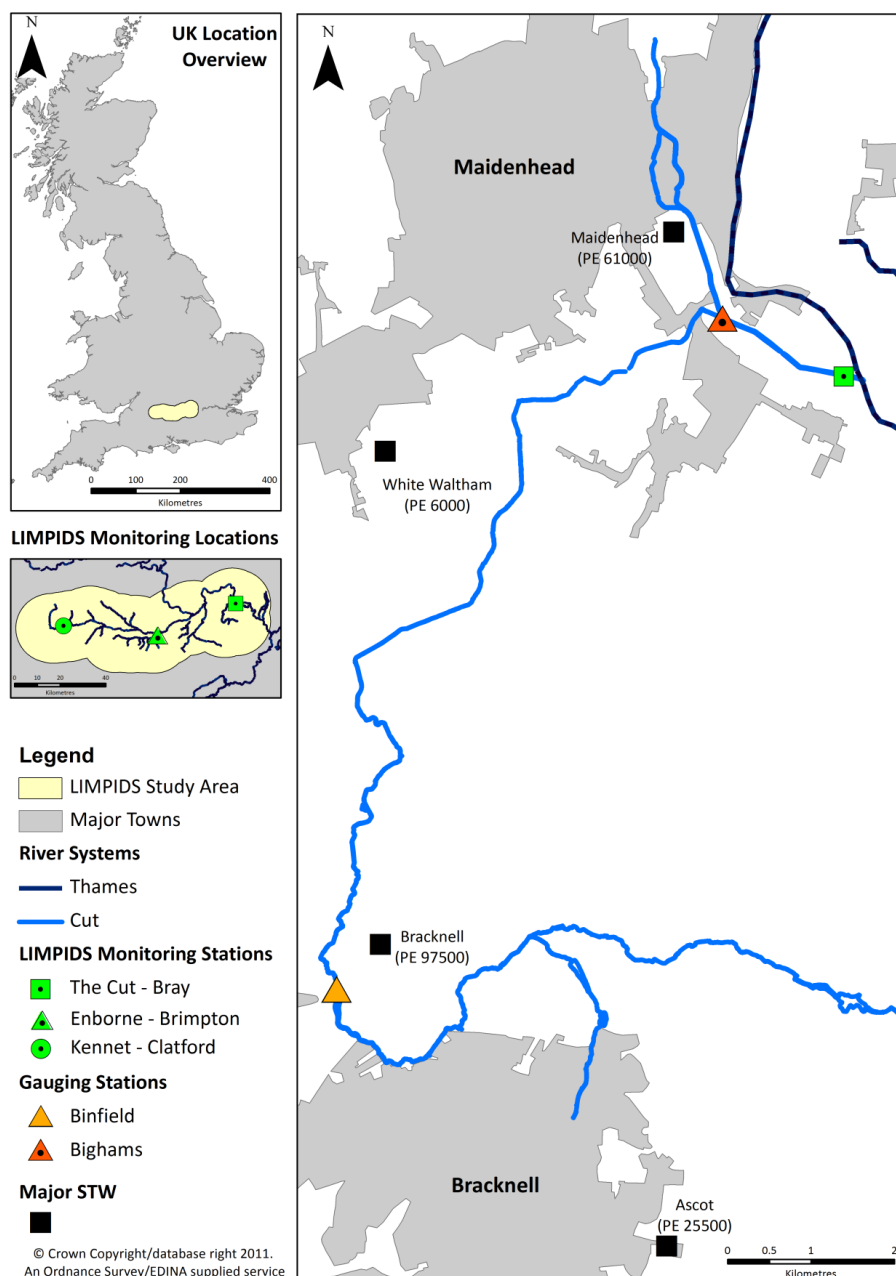


Fig. 2. The Cut study area.

The Kennet catchment is mainly rural, with arable agriculture being the predominant land use. The monitoring site at Clatford, draining an area of 118 km², is located upstream of Marlborough and drains predominantly rural land with a few scattered settlements (Fig. 1). The water quality at Clatford is therefore viewed as not being strongly affected by sewage effluent inputs, though there is a rural STW approximately 1 km upstream at Fyfield, which serves a PE of 1700 (Fig. 1).

2.3 The Cut at Bray

The Cut rises in gravels to the north of Bracknell, drains an area of 85 km², and flows northeastwards to join the River Thames at Bray, near Maidenhead (Fig. 2). Discharge is measured in The Cut at Binfield, which is approximately 10 km upstream of the monitoring site at Bray, and water level is measured at Bighams. The mean daily flow was 0.39 m³ s⁻¹ measured from 1957 to 2005 (Marsh and Hannaford, 2008). The geology is predominantly London Clay and Reading Beds (Palaeocene clays and sands), and the land

use is mainly rural in the headwaters, but dominated by urban development in the mid and lower reaches. The base flow index is 0.46. The Cut drains the town of Bracknell and southern and western Maidenhead with large sewage works discharging treated sewage effluent to the main channel and tributaries at Maidenhead (PE 61 000), Bracknell (PE 97 500) and Ascot (PE 25 500), which are approximately 3, 10 and 15 km upstream of the monitoring site at Bray, respectively (Fig. 2). The flow in The Cut is affected by balancing ponds within Bracknell (to manage storm event runoff) and the result of the river being artificially diverted eastwards from its original course.

3 Methodology

Each of the three study sites was instrumented with a YSI multi-parameter 6600 sonde and a high-frequency nutrient monitor in October 2009. The instrumentation was programmed on-site initially and then remotely using a Meteor Burst system from Meteor Communications (Europe) Limited (Meteor Communications, 2011). The instrumentation was connected to the Environment Agency/Meteor Communications sensor web network. The measurements were transmitted by the telemetry system and were accessed in real-time through a web host.

The YSI 6600 sondes measured *in situ* dissolved oxygen, pH, water temperature, conductivity, turbidity and chlorophyll concentration. All methods are described in the YSI manual (YSI, 2007). Turbidity measurements were automatically temperature compensated and made using a light scattering technique at a wavelength between 830–890 nm and reported as nephelometric turbidity units (NTU). Chlorophyll was measured by a fluorometer at 470 nm and reported as $\mu\text{g l}^{-1}$ of total chlorophyll (*a*, *b* and *c*). As the sensor measured fluorescence, it was subject to optical interference from sediment, however, these sensors were shown to provide a good correlation with chlorophyll measurements made from grab samples and the interference effect was accounted for in the data analysis through comparison with the turbidity data. The YSI sondes were calibrated every 2–3 weeks following standard operating procedures.

Three different types of high-frequency nutrient monitors were used: the Systea Micromac C, the Hach Lange Phosphax Sigma and the Hach Lange Nitratex. Details on the specific set-up of the instrumentation used at each site are given in Sects. 3.1 to 3.3. Water quality monitoring commenced on 1 November 2009 and was ongoing on the Enborne and The Cut at 31 March 2012.

3.1 The River Enborne at Brimpton

A Micromac C automated nutrient analyser (Systea S.p.A, Anagni, Italy), a YSI 6600 sonde and a Nitratex Plus probe (Hach Lange G.M.B.H., Düsseldorf, Germany) were

installed in the River Enborne at Brimpton and each instrument was set to make hourly measurements. The instrumentation was housed in an insulated wooden shed, 2 m from the riverbank (Fig. 3a). Water was pumped from an intake point in the river, 1 m from the riverbank, using a peristaltic intermittent pump, and passed through a flow cell in which the YSI sonde was placed. Continuous pumping caused sediment resuspension within the flow-through cell, making turbidity readings unreliable, and therefore intermittent pumping was used. Water was pumped into a smaller adjacent flow cell from which the Micromac C drew samples through black tubing (1.5 mm internal diameter) using a peristaltic pump. The tubing was black to exclude light and prevent algal growth. The Micromac C uses colorimetric methods to determine unfiltered, molybdate-reactive phosphorus (Total Reactive Phosphorus, TRP), nitrite (NO_2) and ammonium (NH_4). TRP is an operationally defined measurement and is predominantly comprised of orthophosphate (PO_4) and readily hydrolysable P species. TRP was analysed using a method based on phosphomolybdenum blue complexation (Murphy and Riley, 1962) and the detection limit was $0.025 \text{ mg P l}^{-1}$; NO_2 was measured at 525 nm after reacting with sulphanilamide and N-(1-naphthyl) ethylenediamine (NEDD) in acid to give a diazonium salt; and NH_4 was measured by a modified Berthelot reaction using salicylate to measure NH_4 (Krom, 1980). There was no filtration step in the analyses. The instrument measured a check standard daily and was manually recalibrated when the reagents were changed on a fortnightly basis. There is no 06:00:00 GMT sample throughout the entire dataset for TRP, NO_2 or NH_4 since this is when the instrument measured a check standard. The instrument requires a 12 V power supply.

The Micromac C generates large volumes of waste water, approximately 100 L every two weeks. This waste was stored in plastic containers before removal from site and the contents disposed of in accordance with CoSHH guidelines at the Centre for Ecology and Hydrology (CEH) Wallingford laboratories. There was mains power at the Brimpton site and the shed was heated by three tubular heaters, controlled by a thermostat set to 20°C . The heating minimised errors associated with reaction temperature and helped to prevent problems associated with frozen sampling pipes.

The Hach Nitratex Plus probe was placed directly in the river and measured NO_3 using a reagent-free, ultra-violet (UV) absorption technique (Hach-Lange, 2007). A built-in photometer measured the primary UV 210-nm beam, while a second beam of UV light at 350 nm provided a reference standard and a correction for interference caused by turbidity and organic matter. The Nitratex probe was tested before deployment using standard solutions in the laboratory and was also removed from the field periodically and checked using a standard solution. The detection limit was 0.07 mg N l^{-1} . Fifteen-minute flow data were supplied by the EA, from the gauging station (River Enborne at Brimpton) immediately adjacent to the sampling location (Fig. 1).



Fig. 3. Photographs of the river monitoring stations. River systems (top row – taken in March 2010): **(a)** River Enborne at Brimpton (Great Britain National Grid Reference, SU56776477), **(b)** River Kennet at Clatford (SU16016885) and **(c)** The Cut at Bracknell (SU85837050). Monitoring stations (bottom row – taken in April 2010): **(a)** River Enborne at Brimpton (SU56776477), **(b)** River Kennet at Clatford (SU16016885) and **(c)** The Cut at Bray (SU91397866).

3.2 The River Kennet at Clatford

A Syssta Micromac C and a YSI 6600 sonde were installed on the River Kennet at Clatford and they were housed in an insulated wooden shed, sited 3 m from the riverbank (Fig. 3b). Monitoring was hourly, with water being pumped from a river intake point 2 m from the riverbank, using a peristaltic pump and passing through a flow cell in which the YSI sonde was placed. As for the River Enborne, water was also pumped into a smaller, adjacent flow cell from which the Micromac C drew samples. The Micromac C at Clatford used the same colorimetric methods as the instrument installed at Brimpton to determine TRP and NO_2 , but used fluorimetry at 880 nm after reacting with a buffered solution of orthophthalaldehyde to measure NH_4 . Again, there was no filtration step in the analysis and the reagents were changed and the instrument recalibrated every two weeks. As at Brimpton, there was no 06:00:00 GMT sample for TRP, NO_2 or NH_4 throughout the entire dataset, since this is when the instrument measured a check standard.

There was no mains electricity at the Clatford site and therefore a propane-fuelled generator provided power for all the instrumentation and was heated by three tubular heaters, controlled by a thermostat set to 20 °C. Fifteen-minute flow data were supplied by the EA, from a gauging station (Kennet

at Marlborough) approximately 3 km downstream of the sampling location (Fig. 1). There are no major tributaries or STW discharges to the Kennet between Clatford and Marlborough, therefore the flow at Marlborough was assumed to be representative of the flow at Clatford.

3.3 The Cut at Bray

A Hach Lange Sigmatrax and Phosphax Sigma and a YSI 6600 sonde were installed at Bray to make hourly measurements of water quality (Fig. 4). The instrumentation was housed in a mobile monitoring unit 5 m from the riverbank, such that the entire system was portable (Fig. 3c). For security reasons, the wheels of the trailer unit were clamped and the trailer was situated at a site with security cameras. Water was pumped continuously from the river into a flow cell in the trailer unit using a submersible pump situated in the middle of the river channel, and the YSI sonde and Hach Lange Sigmatrax sampling probe were placed in this flow cell. The Sigmatrax module is a sampling unit that pushes the sample through a heated tube using positive pressure. The unit then homogenises the sample using an ultra-sonic probe within a glass chamber before a 10 ml sub-sample is transferred to the Phosphax Sigma (Hach-Lange, 2003). The Phosphax Sigma is an in situ, high-frequency instrument that uses colorimetric and digestion methods to analyse for total phosphorus (TP)

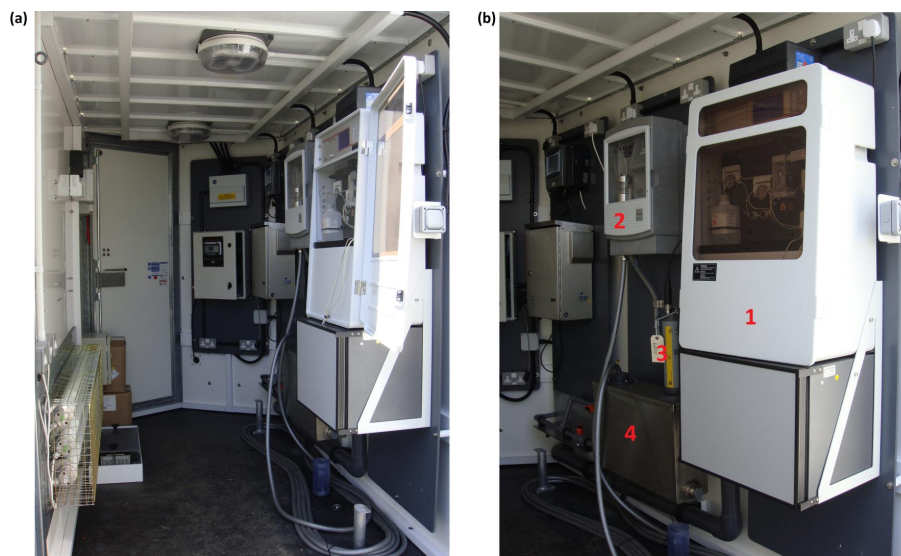


Fig. 4. An internal view of the monitoring station on The Cut taken on 22 April 2010 (SU91397866): **(a)** the layout of the station, with all monitoring equipment housed on the right-hand side and the heater on the left-hand side, and **(b)** close up of the monitoring equipment: (1) Hach Lange Phosphax, (2) Hach Lange Sigmatax, (3) YSI Multi-parameter Sonde and (4) the flow cell where water is pumped to from the river and then samples are extracted for analysis.

and TRP (Hach-Lange, 2002). TP was determined colorimetrically on an acid persulfate digestion after heating to 140 °C, at a pressure of 2.5 bar (359 kPa) using a method based on Eisenreich et al. (1975). TRP was analysed using a method based on phosphomolybdenum blue complexation (Murphy and Riley, 1962). The detection limit of the Phosphax for both TP and TRP is 0.01 mg P l⁻¹. The instrument was validated using standard solutions. A resolution of 0.01 mg P l⁻¹ is shown in Jordan et al. (2005). The Phosphax Sigma ran an automated calibration each day. There was no filtration step in the analysis. The Hach Lange instrumentation requires a 240 V power supply. There was mains power at the Bray site and the trailer was heated by three tubular heaters, controlled by a thermostat set to 20 °C.

The Hach Lange Phosphax Sigma is also capable of determining filtered P fractions: Total Dissolved P (TDP) and Soluble Reactive P (SRP). This analysis follows the same procedure as the TP and TRP analysis for TDP and SRP, respectively, but the analysis is done on a filtered sample. This analysis was trialled in The Cut between November 2010 and January 2011. During this time the TP and TRP analysis was not done. Sample filtration was undertaken using an in situ filtration system, the Hach Lange Filtrax. The control unit was mounted in the trailer adjacent to the Sigmatax and the filtration module was placed directly into the flow cell. Within the filtration module there were two filters that were each spanned by a 0.15 µm membrane. This was a moulded system that could not be changed. An air-purge system underneath the two immersed filters provided a continuous supply of air which automatically cleaned the filter elements by preventing adhesion of solids to the membranes. The samples

were drawn through the immersed membranes via two tube-metering pumps which were housed within the control unit. Filtered samples were then pumped from the control unit to the Phosphax Sigma for analysis. Due to biofouling, all equipment was cleaned every fortnight.

Fifteen-minute flow data were supplied by the EA from the gauging station (The Cut at Binfield) approximately 10 km upstream of the water quality sampling location at Bray. In addition, information on the daily water level at a site 1.5 km upstream of Bray at Bighams was also provided by the EA (Fig. 2). The relationship between the daily mean flow at Binfield and the recorded flow level at the Bighams was highly correlated ($n = 438$; $r^2 = 0.94$; $p < 0.01$). This indicated on a daily basis that the system response was consistent and as such, flow data from Binfield was used within this work as a surrogate for the flow in The Cut at Bray to interpret the water chemistry dynamics in terms of changes in flow (but not to calculate loads).

4 Quality control

4.1 Validation of high-frequency data

Manual streamwater samples were collected at weekly intervals from the main flow of each of the three sites, as part of the CEH Thames Initiative monitoring programme, to validate the high-frequency nutrient data. TRP was determined colorimetrically by the phosphomolybdenum blue method (Murphy and Riley, 1962). TP was digested and determined colorimetrically (Eisenreich et al., 1975). NH₄

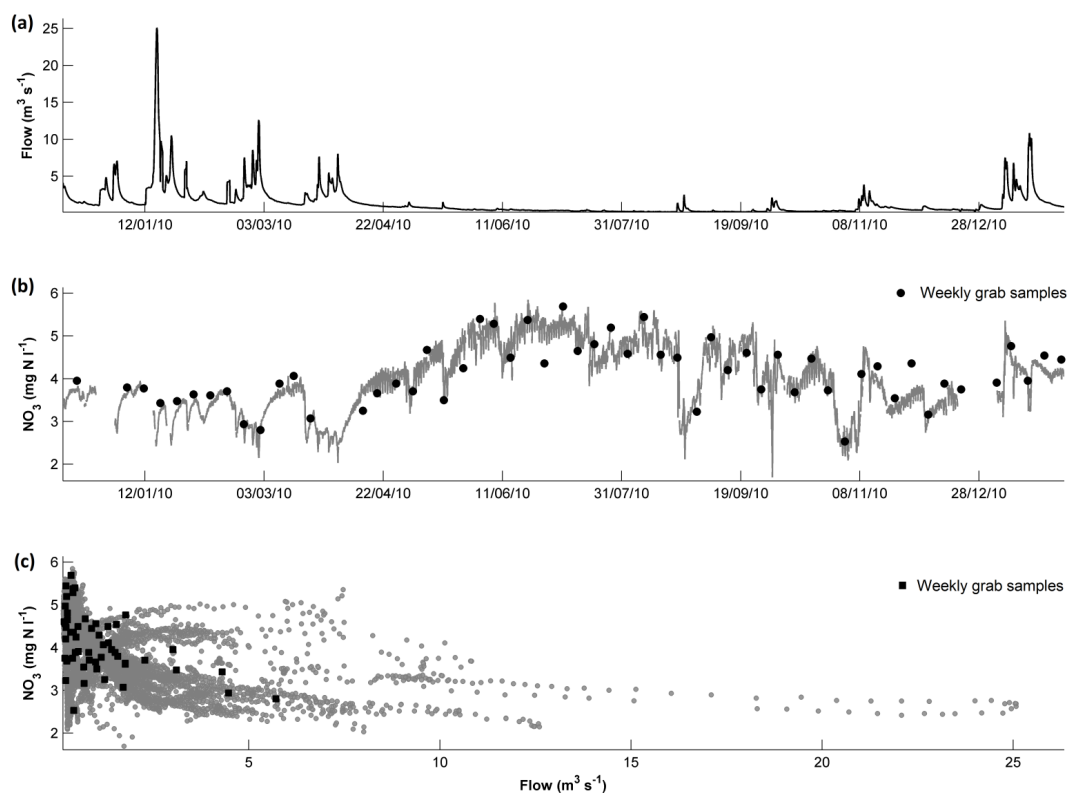


Fig. 5. River Enborne (a) flow ($\text{m}^3 \text{s}^{-1}$), (b) streamwater NO_3 concentration (mg N l^{-1}) and (c) scattergram of streamwater NO_3 concentration and flow.

concentrations were determined colorimetrically using a modified Berthelot reaction (Krom, 1980). Thus the analytical methods to determine TRP, TP and NH_4 were identical to those used in the Enborne and The Cut. Samples for NO_2 and NO_3 were filtered ($< 0.45 \mu\text{m}$) in the field immediately upon sampling and then analysed by ion chromatography (Dionex ED40 Electrochemical detector). Weekly samples were also taken for pH, chlorophyll *a* (determined after extraction into 90 % acetone; HMSO, 1986) and suspended sediment. Conductivity, pH and water temperature were measured weekly in situ using a Myron L Ultrameter II 6P.

4.2 In situ instrument temperature stability

Temperature stability trials were undertaken on the Systea Micromac C and the Hach Lange Phosphax Sigma instruments. Although both sheds were insulated and the sheds and trailer had heaters installed to try to maintain the temperature at 20°C , maintaining a stable temperature within the sheds/trailer during the winter months proved extremely difficult. The operating temperature range for the Micromac C was specified as 8 to 30°C . However, the temperature stability trials revealed that, despite a heating step within the analyses, the determination of TRP was temperature-dependent below 15°C , NO_2 determination was temperature-dependent below 10°C , and that NH_4 concentrations show a linear

correlation with temperature. Hence it was necessary to temperature-correct the results collected by the Micromac C. The Phosphax Sigma analytical measurements did not appear to be affected by changes in ambient temperature. This is due to a more robust and timely heating step during the colorimetric analysis. No temperature correction of the data was thus required for the TP and TRP collected in The Cut.

4.3 The identification of errors in the high-resolution time series data

Following temperature correction of the River Enborne high-frequency data, the high-frequency water quality data collected in both the River Enborne and The Cut show good agreement with the weekly manual samples analysed in the laboratory (e.g. Fig. 5). Detailed log books were maintained for all in situ instrumentation. Each of the continuous water quality data sets was visually assessed to identify any potential anomalies. Any obvious anomalies, such as conductivity readings near zero, were removed. Evident outliers for periods where the probe readings clearly demonstrated instrument drift were also removed. Steps in the data due to calibration changes were relatively common and, where possible, these were adjusted based on the results from the grab samples collected to ground truth the field-based measurements. If there was no justification for point removal, points

were retained. Infilling of the data was not undertaken, all removed points and occasions when sample analysis was not done were retained within the dataset and assigned a missing value code.

4.4 Load estimation using the high-frequency TRP and NO₃ data resampled at different frequencies

A year of hourly TRP and NO₃ data, from December 2009 to December 2010, for the River Enborne was resampled to create five artificial datasets of coarser resolution: 7-hourly, daily, weekly, fortnightly and monthly. The resampled time series were as follows:

- 7-hourly – the first 09:00:00 GMT sample and then every sample at 7 h intervals after that, following the sampling regime employed in recent studies (Jordan and Cassidy, 2011; Neal et al., 2012b);
- Daily – every 09:00:00 GMT sample;
- Weekly – the 09:00:00 GMT sample collected on a Monday;
- Fortnightly – the 09:00:00 GMT sample collected every second Monday;
- Monthly (1st) – the 09:00:00 GMT sample collected on the first day of the month;
- Monthly (11th) – the 09:00:00 GMT sample collected on the eleventh day of the month; and
- Monthly (21st) – the 09:00:00 GMT sample collected on the 21st day of the month.

The resampled datasets were then used to calculate annual nutrient loads using a standard flux-based algorithm based on metrics of instantaneous discharge and concentration (Walling and Webb, 1985; Littlewood and Marsh, 2005; Johnes, 2007; Cassidy and Jordan, 2011; Jordan and Cassidy, 2011):

$$L = \frac{K \sum_{i=1}^n (C_i Q_i)}{\sum_{i=1}^n Q_i} Q_r \quad (1)$$

$$Q_r = \frac{\sum_{j=1}^N Q_j}{N}, \quad (2)$$

where L is the annual load estimate, C_i is the instantaneous determinand concentration (mg l^{-1}), Q_i is the instantaneous discharge at the sample time, i ($\text{m}^3 \text{s}^{-1}$), and Q_r is the average discharge, based on higher frequency discharge records over the period of the load estimate. K is a constant which accounts for the duration of the record. Q_j is the recorded discharge at 15 min intervals, N is the number of flow measurements and n is the number of concentration measurements.

5 Results and discussion

Key initial findings within the high-frequency data have been extracted here, to exemplify the new insights these data can provide about the hydrochemical functioning of complex heterogeneous lowland catchments. Given the problems on the Kennet, only the measurements for the River Enborne and The Cut are considered (see Sect. 5.2). However, it is useful to consider the monitoring in the River Kennet in terms of issues with the instrumentation to provide justification for a move to miniaturised sensor technologies. The information about hydrochemical sources, processes and dynamics which would be missed by sampling at frequencies greater than one day is examined. The suitability of deploying laboratory-based instrumentation into the field is discussed, given the experiences of this study. Based upon our observation and experience, a case is then made for the need for novel, miniaturised field-based water quality sensors.

5.1 Flow and nutrient dynamics – insights gained from high-frequency monitoring

5.1.1 Dynamics in river flow

The hydrological changes provide the context in which the hydrochemical dynamics must be considered. The River Enborne flow responds rapidly to rainfall events, varying over three orders of magnitude from 0.1 to $25.1 \text{ m}^3 \text{s}^{-1}$, with the flow signal dominated by large peaks resulting from the clay geology (EA, 2004). Flow in The Cut is significantly less than in the River Enborne, ranging from 0.06 to $5.4 \text{ m}^3 \text{s}^{-1}$. However, The Cut still exhibits a rapid response to storm events due to the high proportion of urbanisation within the catchment. In the River Enborne and The Cut during periods of low flow, a strong, two-peak flow pattern was identified each day. An example of this pattern is provided in Fig. 6. Although the two periods shown demonstrate a similar flow response within both catchments, with an early morning peak at approximately 05:00:00 GMT and an afternoon peak at approximately 17:00:00 GMT, the phase and amplitude of the diurnal flow cycle is not consistent during every low flow period.

The occurrence of this two-peak cycle is indicative of the dominance of STW discharges on the overall river flow during low flow periods (Radke et al., 2010). STW discharges have been identified to exhibit two peaks each day, linked to periods of greater domestic water consumption in the morning and evening (Pescod, 1992; Palmer-Felgate et al., 2008; Withers and Jarvie, 2008). These daily double peaks, when evident within the stream, lag the actual water usage peak because of the transit time of the water through the STW and because of a further transit between the discharge of the final effluent from the works and arrival at the river monitoring point. Given the distance between the STWs and monitoring point varies from study to study, the timing of the double

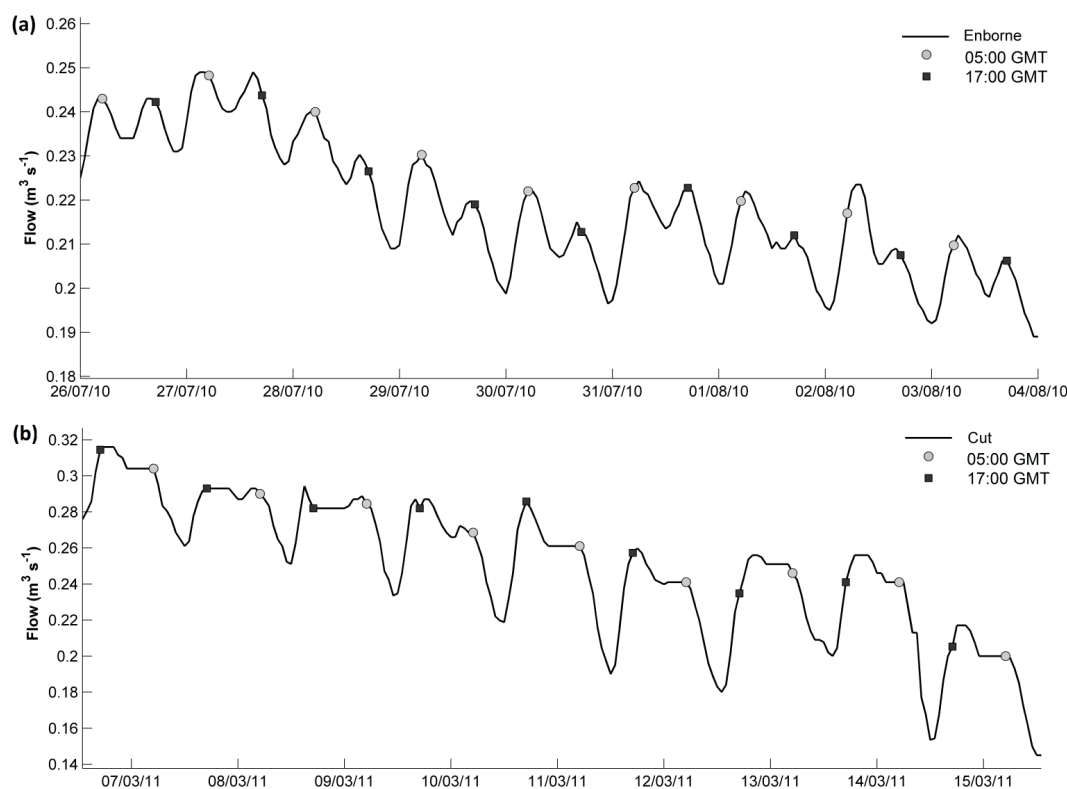


Fig. 6. Two-peak diurnal pattern within the catchment flow time series on (a) the River Enborne and (b) The Cut. For the periods shown, the two catchments are exhibiting a similar phasing in the flow diurnal cycle, with peak flows occurring at either 05:00:00 or 17:00:00 GMT, followed in each case by a secondary peak 12 h later.

peaks will also vary (Palmer-Felgate et al., 2008; Withers and Jarvie, 2008). This result highlights how important the impact of even small STW discharges can be to river systems during periods of low flow, even at distance (7 km) from the works. This result is similar to findings for point source discharges reported in Northern Ireland rural streams by Jordan et al. (2007).

5.1.2 Dynamics in the TRP concentrations

The TRP concentrations ranged from the detection limit of 0.01 to 0.60 mg P l⁻¹ and from 0.2 to 1.45 mg P l⁻¹ on the River Enborne and The Cut respectively. On The Cut, TRP and TP concentrations were strongly correlated with a relationship close to 1 : 1 (Eq. 3; 95 % confidence interval):

$$\begin{aligned} \text{TRP} &= 0.990 (\pm 0.004) \times \text{TP} + 0.052 (\pm 0.003) \\ r^2 &= 0.98 (p < 0.01). \end{aligned} \quad (3)$$

The high proportion of TP that is TRP suggests that P is being delivered to the system from STWs. Overall the TRP time series for the River Enborne demonstrated a weak negative relationship with flow ($r^2 = 0.25$); however, this relationship was not constant, becoming positive during certain high-flow events (Fig. 7a). This complex relationship with flow is indicative of a change in the dominant P source within the

catchment under varying flow conditions. Research over the last ten years in the Kennet river system has shown that, under baseflow conditions, point sources such as STWs, combined sewer overflows and septic tanks that discharge directly into the river are dominant. The constant delivery of P to the system from these sources, results in P concentration increases during periods of low flow due to the reduced dilution capacity of the river (Jarvie et al., 2006; Bowes et al., 2008; Neal et al., 2010). Further work is required to establish the relative importance of each STW, combined sewer overflows and septic tanks discharging directly to the River Enborne. Under high flows, diffuse sources of P, from agricultural fertilisers and from multiple septic tanks acting as a diffuse source, typically become predominant as P delivery increases with increasing flow (Jarvie et al., 2006; Bowes et al., 2008; Neal et al., 2010). The increase in P concentration at high flows may also be caused by the resuspension of bed material (Palmer-Felgate et al., 2009). The sub-daily TRP measurements for the rural River Enborne show that these explanations are based on emergent properties apparent in weekly and fortnightly datasets; sub-daily data reveal a far more complex system with subtle variations in dilution and concentration dependent on the antecedent conditions and bed suspension. The exhaustion of P supply from diffuse

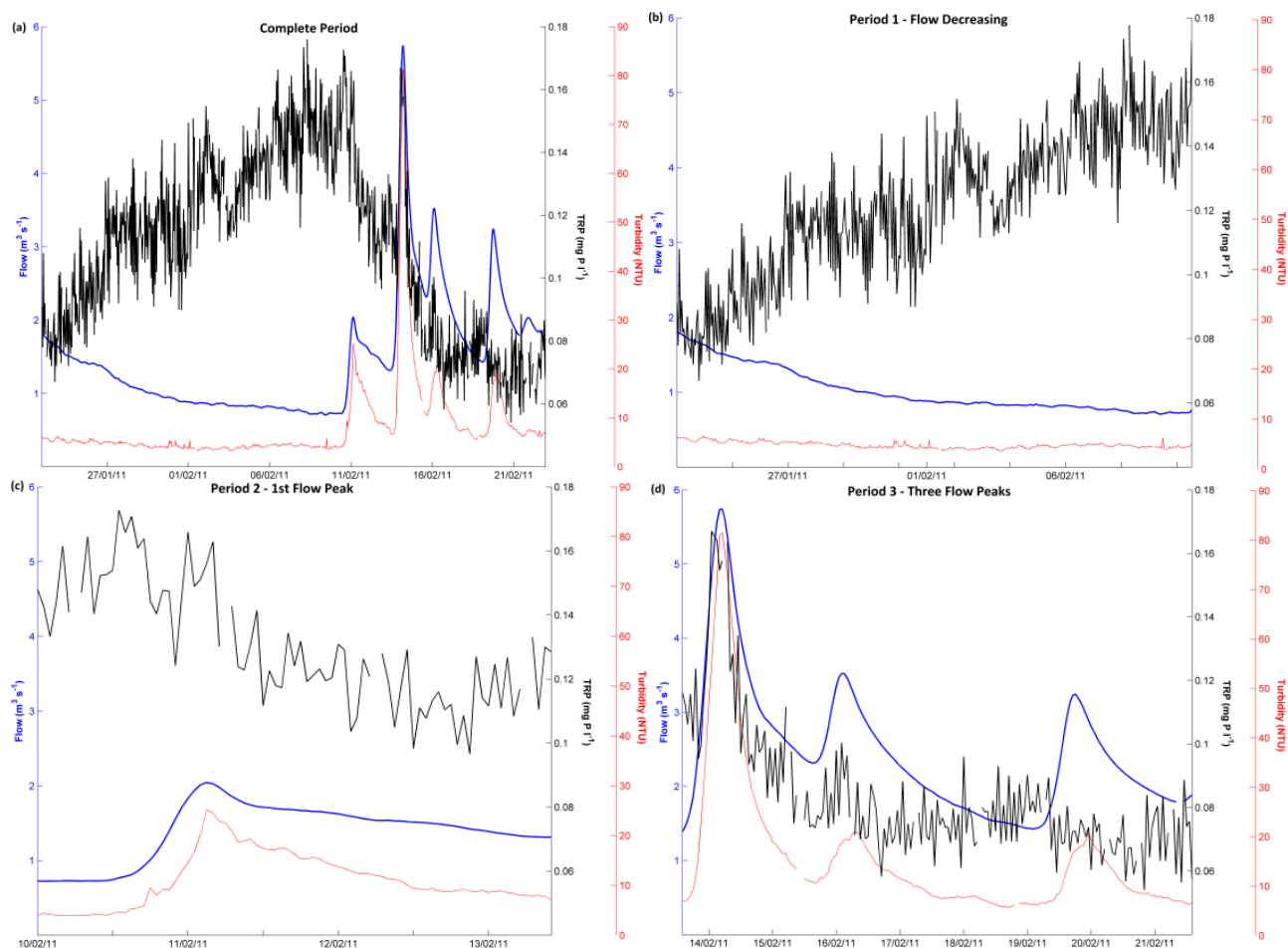


Fig. 7. Streamwater phosphorus dynamics in the River Enborne for a one-month period between January and February 2011. The figure illustrates the complexity of the TRP response to flow events for (a) the period January to February 2011. Panel (b) demonstrates that streamwater TRP can increase as flow decreases during this period. Panel (c) demonstrates an initial dilution of the streamwater TRP followed by a subsequent increase with a peak in flow. Panel (d) illustrates how the streamwater TRP concentration can increase and then decrease with subsequent peaks in flow.

sources was also evident with the TRP concentration falling more rapidly than the receding limb of the hydrograph.

The complexity in response can be seen in the one-month period between 23 January and the 21 February 2011 (Fig. 7a). At the start of the period, flow was in decline following a high flow event at the start of January (Fig. 7b). Although there is a high degree of diurnal variability in the TRP concentration, it is clear that as flows decline there is a steady increase in the streamwater TRP concentration, with TRP and flow exhibiting a significant negative correlation between 23 January and 9 February ($\rho = -0.86$, $p < 0.001$, $N = 426$). This increase in concentration with declining flow suggests that even during this winter period, point sources of P still dominate the stream dynamics. When flow starts to increase on the 10 February there is an initial dilution in TRP concentration, which is followed by a small peak in concentration, then the TRP concentrations start to decline as

the flow declines (Fig. 7c). The initial decrease in concentration is due to the increased dilution capacity of the river as flow starts to increase. The increase in TRP concentration associated with this discharge peak corresponded with a small peak in turbidity, 25 NTU, and this was thought most likely due to mobilisation of sediment from the stream bed since the peaks in flow and turbidity occurred at the same time. After this initial flow peak there were three further flow peaks (Fig. 7d). The largest flow peak, $5.74 \text{ m}^3 \text{ s}^{-1}$, was associated with a large peak in TRP concentration, 0.17 mg P l^{-1} , and a large peak in turbidity, 81 NTU. Again this peak in TRP concentration is likely to be caused by mobilisation of stream bed sediments and possibly also a mobilisation of P from diffuse sources under high flow conditions. After this concentration peak, TRP concentrations decline as the flow declines. The second flow peak of this event also caused a peak in TRP concentration, 0.10 mg P l^{-1} ; however, although

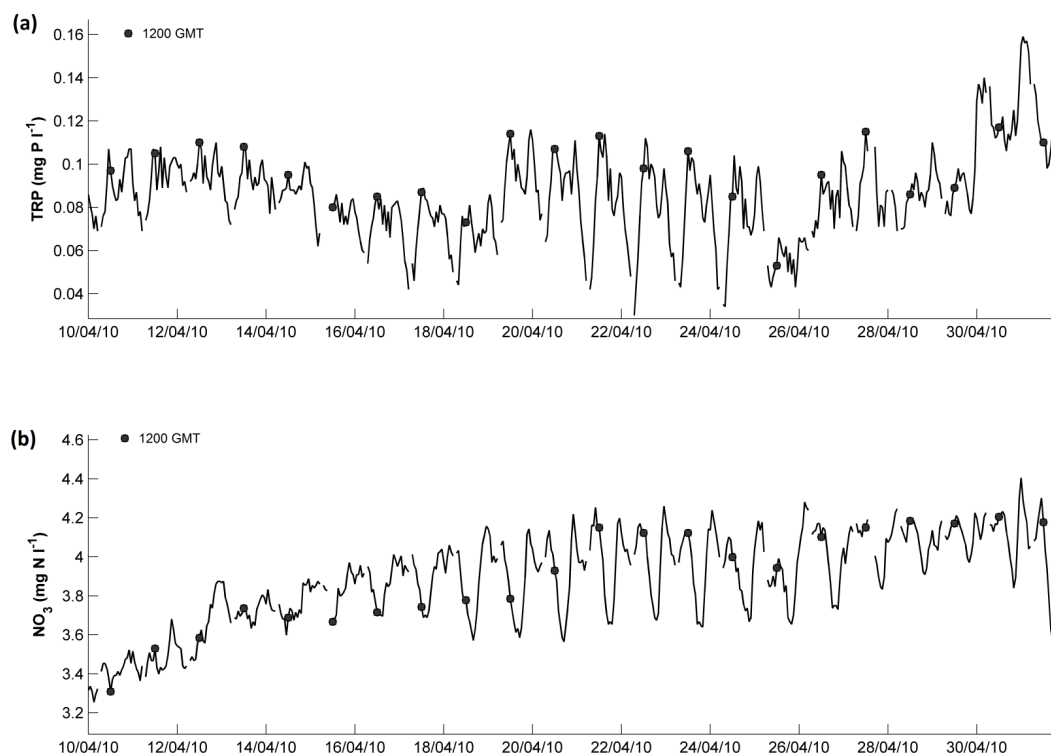


Fig. 8. Two-peak diurnal patterns within the observed streamwater (a) TRP and (b) NO_3 concentrations in the River Enborne.

turbidity increased, the timing was not completely consistent with the flow and this peak in TRP concentration is thought more likely to represent the delivery of P to the stream from diffuse sources. The last flow peak of the period does not cause an increase in TRP, instead the TRP concentration remains in decline following the preceding flow peak (Fig. 7d). This suggests an exhaustion of P supply from diffuse sources during this event, such that the delivery of water causes a dilution in the P being supplied from the catchment point sources. The propensity of this system to switch between point- and diffuse-source domination, dependent on the flow conditions, highlights the complexity involved in managing the system and designing effective P-reduction strategies.

In both the River Enborne and The Cut, strong diurnal cycling was evident in the TRP time series. In both catchments, the amplitude and phase of the diurnal dynamics changed through the study period (Figs. 8 and 9). During low flow periods, a two-peak diurnal cycle in the TRP time series was particularly apparent in the River Enborne (Fig. 8a). The amplitude and phase of this cyclical pattern changed through the study period. The presence of a two-peak diurnal cycle, which strengthens when flow declines, is a further indication of the STW dominance of P inputs within the River Enborne (Palmer-Felgate et al., 2008). This outcome highlights that, even within a predominantly rural catchment such as the River Enborne, diurnal peaks in P concentration were evident due to inputs of final effluent from small STWs within the

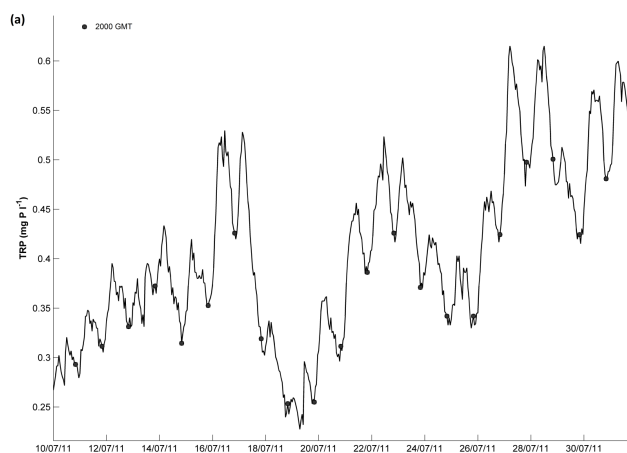


Fig. 9. Diurnal patterns within the observed streamwater TRP concentrations in The Cut.

catchment. This finding contrasts with other work, based on daily monitoring, which attributed the instream SRP concentrations to diffuse contributions with subsequent in-channel processing (Evans and Johnes, 2004). A diurnal pattern in The Cut is also evident under low flow conditions but this tends to have a single, rather than double, peak each day (Fig. 9). The reasons for the different dynamics between the River Enborne and The Cut are not yet clear.

5.1.3 Dynamics in NO₃ concentrations

The NO₃ concentrations measured in the River Enborne ranged from 1.7 to 5.8 mg N l⁻¹ (Fig. 5). The time series showed a seasonal pattern with NO₃ concentrations, initially increasing in the spring to reach an early summer maximum and then a decline through the autumn to reach a winter minimum (Fig. 5b). Streamwater NO₃ concentrations, measured in the River Enborne, exhibited a weak negative relationship with flow ($r^2 = 0.19$; Fig. 5c). This weak relationship arose because of the compound effects of different process and pathways through the year when significant dilutions of NO₃ occurred at high flows, but also increases in NO₃ concentration were evident, for example in January 2011 (Fig. 5b). The seasonal pattern observed in the River Enborne contrasts with that observed in the River Lambourn, where streamwater NO₃ concentrations are highest (approximately 8.5 mg N l⁻¹) in winter and lowest (approximately 6.5 mg N l⁻¹) in summer (Neal et al., 2004). The seasonal pattern, observed in the River Lambourn, is thought due to a combination of increased soil mineralisation in autumn, fertiliser runoff, increased winter groundwater inputs to the river that are enriched with NO₃, and increased crop uptake of NO₃ during the growing season combined with the effects of instream processing. To date, the determination of the relative importance of the different processes and pathways in the River Lambourn has proved challenging (Wade et al., 2006).

The NO₃ signal in the River Enborne was also dominated by a strong complex diurnal cycle, which was strongest during the low flow periods of the spring and summer, reaching amplitudes of 0.6 mg N l⁻¹, and a two-peak diurnal phase was observed at certain periods (Fig. 8b). Again, as with P, this two-peak diurnal cycle, and the seasonal streamwater NO₃ pattern, most likely highlights the importance of STW discharges in a clay catchment considered “rural”. Subtle, compound effects of catchment nutrient sources and processes on streamwater concentrations, in this case potentially from STW inputs and the catchment vegetation, will be challenging to separate, and perhaps most progress will be made with catchment manipulations and experimental catchments that can isolate the effects of different factors.

5.2 Understanding ecological function: instream productivity, photosynthesis and respiration

The dissolved oxygen levels measured in The Cut varied from 50 to 130 % saturation (Fig. 10). The time series showed a strong seasonal pattern with maximum dissolved oxygen levels in the summer months and minimum levels in the winter as a result of lower photosynthesis. Chlorophyll concentrations were also highest in the summer months, with concentrations of 93 µg l⁻¹ reached. Although this is high, the concentrations were not as high as those recorded for major blooms in parts of the lower River Thames, which has a long residence time due to the large number of locks and

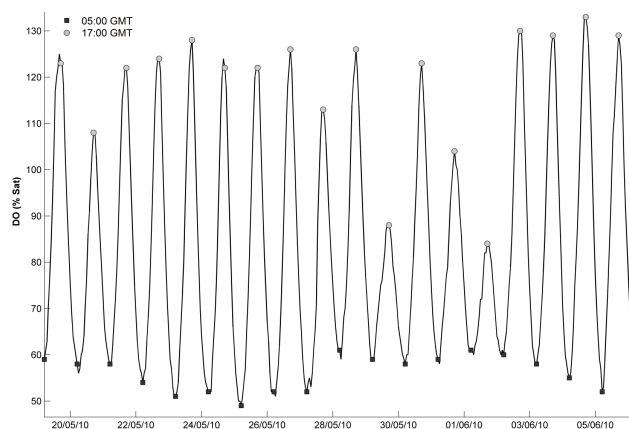


Fig. 10. Diurnal cycling observed within The Cut dissolved oxygen time series, with peak saturation levels in the late afternoon, 17:00:00 GMT, and minimum saturation in the early morning, 05:00:00 GMT.

weirs. Also, a large proportion of the primary productivity in The Cut is periphyton and therefore not measured as suspended chlorophyll. The lack of major algal blooms within The Cut is likely due to a short residence time of the river water due to flushing with inputs of water from Bracknell STW and riparian shading (Bowes et al., 2012a,b).

The dissolved oxygen time series from The Cut was analysed to determine daily photosynthesis and respiration rates using a combination of the “dark hours” and “Delta” methods (Williams et al., 2000; Palmer-Felgate et al., 2008). Both the calculated respiration and photosynthesis display a seasonal cycle with peak rates occurring in the late spring to early summer, and the rate of respiration was greater than the rate of photosynthesis, indicating a heterotrophic system (Odum, 1956; Williams et al., 2000). The rate of both photosynthesis and respiration declined from spring and early summer to winter, possibly as much of the respiration results from the decomposition of primary production, or possibly due to the microbial breakdown of organic material from STW final effluent (Palmer-Felgate et al., 2008). The result that the respiration and photosynthesis estimates both decline in late summer and through the autumn also suggests that the photosynthetic oxygen is derived from algae rather than macrophytes. The latter are expected to photosynthesise for longer than evident in the estimates for The Cut, rather than decline after early summer. The suggestion that algae, rather than macrophytes, control photosynthesis contrasts with the finding of Palmer-Felgate et al. (2008), who suggest aquatic plants control photosynthesis in the upper reaches of the River Kennet. There is no obvious link between the rate of photosynthesis and chlorophyll concentrations in The Cut; the rates of photosynthetic oxygen production are also higher than expected, given the present concentrations of chlorophyll (Krause-Jensen and Sand-Jensen, 1998). This result is

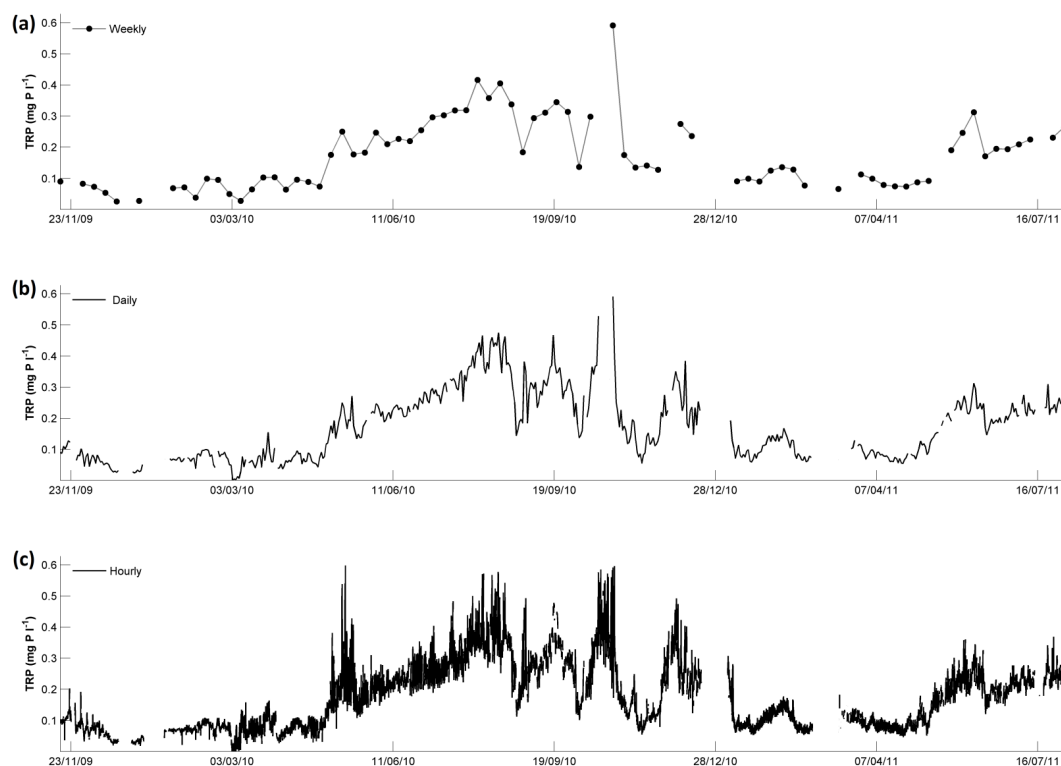


Fig. 11. Streamwater TRP concentrations, observed in the River Enborne, resampled onto lower frequencies to demonstrate the reduction information content as the sampling frequency decreases: (a) weekly, (b) daily and (c) hourly.

due to the importance of periphyton and that the chlorophyll probe measures suspended algae only (Flynn et al., 2002).

5.3 Implications for weekly, fortnightly and monthly water quality sampling

The field-based, hourly measurements of N and P concentration show a greater range than the weekly grab samples used to verify the field-based monitors (Fig. 11). Thus, whilst there are numerous studies which show that weekly samples can be used to elucidate the seasonal and flow response of nutrients, the hourly data reveal a greater variability in the water quality during storms. The timing of sample collection during the low-frequency sampling program is critical to the information content of the resultant dataset time series. For example, on The Cut, the dissolved oxygen time series was dominated by a strong diurnal cycle with peak saturation occurring between 17:00:00–19:00:00 GMT followed by minimum saturation between 05:00:00–07:00:00 GMT (Fig. 10). The difference in saturation levels between these two points varied by 75 percentage points, taking the system from undersaturated at night to supersaturated during the day. Similarly, TRP concentrations in the River Enborne showed rapid decreases greater than $100 \mu\text{g P l}^{-1}$ between 12:00:00 and 17:00:00 GMT (Fig. 8a). The time of sample collection is therefore critical in determining how the chemical status of

the river is interpreted. This is important given the dependence of the WFD on chemical and ecological thresholds to define the status of a water body. Furthermore, by sampling at a frequency which is insufficient to capture the highest frequency component of the nutrient dynamics, errors such as spectral aliasing can occur when using frequency domain analysis (Siren and Vantsi, 2002; Harris and Heathwaite, 2005; Kirchner, 2005; Chen et al., 2006a; Johnson et al., 2007; Halliday et al., 2012).

To gain a true understanding of the hydrochemical dynamics, the sub-daily water quality data need to be used alongside ongoing, long-term low-frequency (fortnightly) monitoring, experiments and manipulation studies to determine the key processes operating (Halliday et al., 2012) or filters applied to high-frequency data to mimic a reduction in sampling frequency. It is only through a good working knowledge of the catchment and previous (weekly or fortnightly) monitoring campaigns that the high-frequency data can be interpreted initially. However, building on this baseline, high-frequency data are invaluable for creating a nuanced level of process understanding, in particular regarding storm dynamics and instream chemical and biological processing.

Load estimates

Previously sub-daily water quality data have been used to estimate loads more accurately (Bowes et al., 2009b; Rozenmeijer et al., 2010; Jordan and Cassidy, 2011) and determine the processes operating (Palmer-Felgate et al., 2008). The results of this study show that resampling the hourly data from the River Enborne at 7 h and daily frequencies does not worsen annual load estimates of TRP and NO₃ compared to estimates based on daily sampling (Table 1). Recent studies have demonstrated the high proportion of nutrient load that is delivered to agricultural river systems during storm events, therefore low-frequency sampling regimes may provide a biased sample, dependent on whether or not high flow events have been captured (e.g. Jordan et al., 2005; Cassidy and Jordan, 2011; Jordan and Cassidy, 2011). In these cases, sub-daily sampling is necessary to fully quantify nutrient delivery. In the case of the River Enborne, the predominant source of TRP is STWs and therefore TRP delivery and in-stream load are not controlled by the occurrence of high flow events, unlike the more agricultural systems studied by Jordan et al. (2005) and Rozemeijer et al. (2010). The reduction in streamwater NO₃ to an asymptotic concentration at high flows means that the NO₃ concentration changes little in the River Enborne in the higher flow range (10–25 m³ s^{−1}), which means a daily concentration is representative of the hourly values in that day (Fig. 5c). Only when the frequency drops to weekly or fortnightly sampling does the load estimate worsen. The annual load estimate based on monthly resampled concentration data is similar to those based on the hourly, 7 h and daily sampling frequencies, when the first and eleventh day in each month was used for the concentration estimate. This was a chance occurrence as resampling based on the 21st day each month gave annual loads 39 and 36 % different from those calculated using hourly sampling for TRP and NO₃, respectively.

5.4 The practicalities and challenges of in situ monitoring

This study attempted to take existing laboratory-based technologies and deploy these in the field for P and also for NO₃, NH₄ and NO₂ and with accompanying measurements of turbidity, chlorophyll, dissolved oxygen, conductivity and pH. Thus, this study takes the work of Jordan et al. (2005, 2007) further by trying to use bank-side P and N analysers that are portable, or without mains electricity, and investigates the potential of in situ filtration. Mobile, in situ “laboratories”, such as the trailer system installed on the The Cut, give the potential to investigate high-frequency dynamics at a range of locations across a catchment and therefore be embedded within a sensor-web network.

The initial installation and ongoing maintenance of the in situ monitoring stations was laborious and expensive. A large amount of resources was invested in identifying suitable sites

Table 1. Annual load estimation, to three significant figures, based on data of differing resolutions from the River Enborne.

	Load estimate		Diff. from hourly load estimate	
	TRP (kg P yr ^{−1})	NO ₃ (kg N yr ^{−1})	TRP (%)	NO ₃ (%)
Hourly	3320	120 000	–	–
7 h	3320	121 000	0.1 %	0.7 %
Daily	3290	120 000	−0.9 %	−0.1 %
Weekly	4170	142 000	26 %	18 %
Fortnightly	4300	139 000	29 %	15 %
Monthly (1st)	3200	123 000	−4 %	2 %
Monthly (11th)	3100	114 000	−7 %	−5 %
Monthly (21st)	2000	76 800	−39 %	−36 %

to install the monitoring stations and designing appropriate structures within which to house the instrumentation. Factors such as site suitability in terms of security, mains power, safety and accessibility, location within the wider Thames catchment, and the availability of flow data and historical hydrochemical data for the site all had to be considered. This necessarily restricted the number of viable locations. As such compromises had to be made, such as locating The Cut monitoring point at Bray, where the site was secure, had mains power and provided valuable information on the streamwater chemistry directly before the rivers confluence with the Thames, but where the nearest discharge gauging station was 10 km upstream. Once installed, the instruments were visited each fortnight for calibration and the collection of a grab sample for comparison. The real-time data were reviewed on a daily basis to identify issues with the equipment, such as pump failures, and facilitate rapid resolution.

The broader EA sensor-web network, in which the instruments were embedded, proved a reliable and robust way to transmit the data for storage on a database. Quality controlling the data was a time-consuming task and needed to be done by an expert. It was very difficult to automate the quality control process, since the errors were not necessarily consistent, and separation of outliers and real extremes proved difficult. Given the volume of data generated by hourly monitoring campaigns, data clean up and analysis appears one of the greatest limitations to the implementation of high-frequency monitoring generally. However, there are rich rewards to be found in the data when this is done, as highlighted by the surprising insights this data offers into the hydrochemical dynamics within the rivers studied here.

A lack of mains electricity prevented successful implementation of the in situ instrumentation on the River Kennet at Clatford. The use of the propane-fuelled generator to power the instrumentation proved unsustainable due partly to wear and a high draw on current which caused high fuel consumption. This was initially combated by reducing the sampling frequency to every two hours, instead of every hour. However, during the winter months there was still insufficient

power to run both the instrumentation and the shed heater, so the heater was turned off. The low winter air temperatures (which fell to -7°C), during the winter of 2009/2010 caused the water in the glass and quartz fluorometer flow cells to freeze, causing each to crack. Furthermore, the measurements made at this site were unreliable given the extensive need for temperature correction. This outcome highlights the need for a reliable power supply for field-based analytical instruments and the provision of heating to regulate the temperature for wet chemistry techniques done in the field. When power is available, and the infrastructure is able to provide a warm, or ideally temperature-controlled laboratory, then wet chemistry can be done in the field as evidenced by the data collected in the River Enborne and The Cut. Following successful development in this study, this type of mobile monitoring system has now been adopted for use in the Department of Environment, Food and Rural Affairs (DEFRA) and EA Demonstration Test Catchment (DTC) programme.

In situ sample filtration also proved extremely difficult in The Cut. Despite the air-purge system within the Filtrax filtration module, the filters still became clogged. This prevented sample extraction and consequently the determination of filtered P fractions, SRP and TDP, was not possible. This is frustrating from a hydrochemical perspective as it is often the concentration of the dissolved P fraction, SRP, which is of most interest because it is considered equivalent to bioavailable P (Nurnberg and Peters, 1984), and can provide an indication of the importance of sewage effluent discharges within a system as SRP correlates well with effluent markers and population density (Neal et al., 2012). In the UK, water quality P standards are also generally set in terms of SRP concentrations (Neal et al., 2010; Palmer-Felgate et al., 2008; Bowes et al., 2012b). Although some studies have shown a close correlation between TRP and SRP concentrations (Palmer-Felgate et al., 2008), this correlation is unlikely to be the case in every system, particularly where the particulate component of TRP is high.

Commercial sensors are available for temperature, pH, electrical conductivity, dissolved oxygen and chlorophyll, and also for some ionic species such as NO_3 and NH_4 . Ion-selective electrodes can, in principle, be constructed for many other species but have, in practice, been of limited use for environmental applications because of problems with fouling, limits of detection, probe drift and lack of robustness. As demonstrated in this study, multi-parameter sondes now provide robust in situ measurements of pH, conductivity, dissolved oxygen, turbidity, water temperature and chlorophyll and high quality datasets have been collected by the EA at 46 sites across the Thames region. These data provide valuable evidence of pollutant inputs, allowing compliance monitoring and, when a chlorophyll probe is deployed, providing early warnings of algal blooms (Lee et al., 2005; Palmer-Felgate et al., 2008). Calibrating and maintaining the electrodes and the sondes are major tasks, requiring trained technical staff, and reliable instrumentation and power supply.

There is still some way to go before NO_3 and NH_4 probes can be considered to give reliable results due to biofouling and, as the case with chlorophyll in this work, interference from sediment. Furthermore, ion-electrode sensors respond to other ions in addition to the one measured, due to an interaction of ion species in the sensor membrane; this is one of the causes of accuracy issues (YSI, 2007). The Nitratax uses UV absorbance and the ambient temperature range is 2 to 40°C . The minimum streamwater temperature in the River Enborne was 0.2°C and the first percentile of the distribution was 1.3°C , so there may be an effect at the lowest temperatures measured, for a total of 109 h during the early mornings of November and December 2010, but otherwise a temperature effect is not expected. Further work is needed to check if there is a temperature effect during extreme cold periods.

Overall the results show that the use of field-based laboratory instrumentation is highly beneficial but, based on the experiences of deploying and maintaining the equipment in this study, it is ultimately not recommended as a best practice because the laboratory equipment is expensive, heavy on reagent use, produces large volumes of waste water, requires additional infrastructure to be portable (the trailer), is vulnerable to vandalism and theft, and most importantly requires mains electricity, which is perhaps the most restrictive factor in terms of sampling location. Also, a large amount of staff time and capital were spent on providing the infrastructure to house the equipment.

If high-frequency hydrochemical monitoring is to become commonplace, new technologies are needed to overcome the practical, scientific and financial restrictions that currently inhibit monitoring of this nature (Kirchner et al., 2004; Neal et al., 2012b). Over the last few years, microfluidic devices have been shown to be capable of making analytical measurements to acceptable levels of accuracy and precision in a number of laboratory-based environmental applications (Marle and Greenway, 2005; Chen et al., 2006a; Richardson and Ternes, 2011; Jokerst et al., 2012). Integrated chips with separation and detection have been developed (and even used in the field) to measure streamwater P concentrations (Kang et al., 2001; Bowden et al., 2002a; Chen et al., 2006b). Most of the work on developing environmental methods for field applications has involved sensors or microfluidic devices for single analytes, or new miniature in situ water samplers, where the sample is recovered and analysed using conventional laboratory instrumentation (Bowden et al., 2002b; Datta and Banerjee, 2007; Gkritzalis-Papadopoulos et al., 2012; Jokerst et al., 2012). For field use, a lab-on-a-chip device of this nature offers huge potential advantages over existing in situ continuous monitoring technologies, because of robustness, reduced power and reagent requirements, reduced waste burden, and the capability to be hidden discretely to minimise interference by vandals (Ramirez-Garcia et al., 2008; Jokerst et al., 2012). The nature of these lab-on-a-chip devices would also mean that multiple locations throughout a catchment could be monitored easily within the

framework of an integrated sensor network. Thus such devices would not only improve the temporal resolution of the hydrochemical data collected, but also the spatial resolution and facilitate real-time monitoring and rapid analysis of water quality along a river continuum. However, further work is needed to produce critical comparisons with existing technologies, such as the wet chemistry platforms described here, across a range of river types. In particular, it is necessary to establish detection limits and the susceptibility to biofouling. The time period for which miniaturised devices can be deployed should also be compared against those methods that show a robust, accurate and sustained data run in complex and challenging river systems.

6 Conclusions

High-frequency data provide significant benefits to the understanding of catchment hydrochemical sources and behaviour. The sub-daily TP, TRP and NO_3 concentrations show that complex, erratic and compound behaviours are evident and these are not captured by daily and less frequent sampling. The sub-daily results show both increases and decreases of streamwater NO_3 concentrations during storm events in the River Enborne, and similarly multiple dilutions and concentrations of P. This outcome indicates that the dominant mode of nutrient delivery to the system switches as a function of antecedent conditions, nutrient supply and the suspension of bed material. The dominance of STW effluent on the instream nitrogen and phosphorus concentration dynamics at low flows was evident in a rural catchment at the monitoring point, approximately 7 km downstream of a small effluent works. Given the diurnal patterns evident, the time when a sample is taken will affect the concentration summary statistics and this should be accounted for when judging water quality against ecological thresholds or standards. Preliminary results for the highly phosphorus enriched river, The Cut, highlight suggest a dominance of algae controls the photosynthesis and respiration dynamics. Daily data appear adequate for annual load estimation in these two catchments, which are STW effluent dominated.

Whilst the example data demonstrate clearly how existing in situ water quality monitoring equipment can detail the hydrochemical dynamics for a small range of analytes, the work also highlights the challenges faced in the running of laboratory analytical equipment deployed in the field. As an alternative, we suggest the development of novel, micro-scale technologies which have much lower power and reagent consumption. These developments offer the prospect of revolutionising hydrochemical monitoring through cost-effective and simultaneous measurement of a wide suite of analytes, as part of a spatially distributed sensor network deployable at remote locations.

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