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From existing in situ, high-resolution measurement technologies to lab-on-a-chip – the future of water quality 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, seemingly chaotic, 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 works in the rural, River Enborne, and that 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 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 dominance of respiration over photosynthesis in The Cut indicated a prevalence of heterotrophic algae, and the seasonal patterns in respiration and photosynthesis corresponded with those of temperature and light in this nutrient over-enriched stream. These results highlight the utility of sub-daily water quality measurements but the deployment of modified wet-chemistry technologies into the field was limited by mains electricity availability. A new approach is therefore needed to allow measurement of a wide range of analytes at a broader range of locations for the development of water

quality web-sensor networks. The development and field deployment of a miniaturised "lab-on-a-chip" ion chromatograph is proposed and justified.

1 Introduction

The chemical and ecological status of surface waters is an increasing concern worldwide as demand for water and food grows as 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 and 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 the ecological structure and 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 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., 2012a, b). 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, southwest 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 (Neal et al., 2012b). 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 the short-term dynamics when the instream biological response is likely to be most evident (Horsburgh et al., 2010; Neal et al., 2012b).

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). The data generated from these in situ studies have been used to demonstrate the benefits of high frequency sampling in areas such as load estimation accuracy (Rozemeijer et al., 2006; Jordan and Cassidy, 2011). 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 quality has been limited to a handful of studies (Jordan et al., 2005, 2007; Scholefield et al., 2005; Palmer-Felgate et al., 2008; Rozenmeijer et al., 2010). These studies have tended to focus on specific nutrients, such as phosphorus (P) or nitrogen (mainly as NO_3), in rural catchments. 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 methods. 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 UK Environment Agency (EA). Of the two sites, the 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 water quality dynamics of these sites, this paper also considers the challenges associated with running analytical instrumentation in the field and details the methodologies. A case is made for the development of a novel miniaturised sensor, based on ion chromatography, to overcome the identified limitations of deploying current laboratory instruments to monitor freshwaters.

2 Study areas

Three monitoring sites were established in the catchment of the River Thames (9948 km^2 measured to the tidal limit at Kingston upon Thames), a major river-system in southern and eastern England (Fig. 1). The three sites were the Enborne at Brimpton, the Kennet at Clatford and The Cut at Bray. Of these sites, good water quality datasets were obtained for Enborne at Brimpton and The Cut at Bray. The monitoring of the water quality in the Kennet at Clatford 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- and ground-water of the Thames is an important regional resource providing water for most of the 20 million people that live within the catchment. The quality of this water resource 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 with 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 km^2 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 than for other, 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) 610, 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. Further works are also located at Washwater on the Pound Street Brook (PE 6600) and at Kingsclere on the Kingsclere Brook (PE 3900), and there are two minor works at Wolverton Townsend (PE 60) and Ashford Hill (PE 40) on the Baughurst Brook. All enter the River Enborne upstream of the Brimpton monitoring site (Fig. 2). The water quality of the Enborne, in terms of suspended sediment and P fractions, was studied by Evans and Johnes (2004) and 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 km^2 and is a major tributary of the River Thames (Fig. 1). The River Kennet flows broadly eastwards for around 40 km before entering the Thames at Reading. Cretaceous Chalk covers approximately 80 % of the catchment. The Kennet catchment is mainly rural, with arable agriculture being the predominant land use. The monitoring site at Clatford, draining an area of 118 km^2, 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 sewage works approximately 1 km upstream at Fyfield which serves a PE of 2080 (Fig. 2).

2.3 The Cut at Bray

The Cut rises in gravels to the north of Bracknell, Berkshire, drains an area of 85 km^2, and flows northeastwards to join the Thames at Bray, near Maidenhead (Fig. 1). The only flow gauge on The Cut is at Binfield which is approximately 10 km upstream of the monitoring site at Bray. The mean daily flow was 0.39 m^3 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 Cut drains the town of Bracknell and southern and western Maidenhead and there are 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 Marina, respectively (Fig. 2). The flow in The Cut is affected by balancing ponds within Bracknell to manage storm event runoff and as a 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). Subsequently, the instrumentation was controlled by a Meteor Communications data node, connected in real time to the Environment Agency/Meteor Communications sensor web network. The measurements were transmitted by the same 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 of between 830–890 nm and reported as nephelometric turbidity units (NTU). Chlorophyll was measured in vivo by a fluorometer at 470 nm and reported as $\mu g\,l^{-1}$ of total chlorophyll (*a*, *b* and *c*). As the sensor measured fluorescence and not chlorophyll directly, it was subject to optical interference, however, these sensors were shown to provide a good correlation with measurements made from grab samples and the interference effect can be accounted for in 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 Nitratax. 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 Enborne at Brimpton

A Micromac C automated nutrient analyser (Systea S.p.A, Anagni, Italy), a YSI 6600 sonde and a Nitratax Plus probe (Hach Lange G.M.B.H., Düsseldorf, Germany) were installed at Brimpton and each instrument was set to make hourly measurements. The instrumentation was housed in an insulated wooden shed, 2 m from the river-bank (Fig. 3). Water was pumped from an intake point in the river, 1 m from the river-bank, using a peristaltic intermittent pump, and passed through a flow cell in which the YSI sonde was placed. Continuous pumping caused sediment re-suspension within the flow through cell making turbidity readings unreliable. Instantaneously, 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 the phosphomolybdenum blue complexation (Murphy and Riley, 1962); NO_2 was measured at 525 nm after reacting with sulphanilamide and N-(I-naphthyl) ethylendiamine (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 auto-calibrated daily and was manually recalibrated when the reagents were changed on a fortnightly basis. There is no 06:00 GMT sample throughout the entire dataset for TRP, NO_2 or NH_4 since this is when the instrument auto-calibrates. The instrument requires a 12 V power supply.

The Micromac C generates large volumes of waste water, approximately 100 l every two weeks, which was stored in plastic containers before removal from site and the contents disposed of in accordance with CoSHH guidelines at the 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 Nitratax Plus probe was placed directly in the river and measured nitrate (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. Fifteen minute flow data were supplied by the EA, from the gauging station (Enborne at Brimpton, 39025) immediately adjacent to the sampling location (Fig. 2).

3.2 The Kennet at Clatford

A Systea Micromac C and a YSI 6600 sonde were installed at Clatford and they were housed in an insulated wooden shed, sited 3 m from the riverbank (Fig. 3). Monitoring was hourly with water being pumped from a river intake point, 2 m from the riverbank, using a peristaltic pump and passed through a flow cell in which the YSI sonde was placed. As at Brimpton, 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 ortho-phthalaldehyde (OPA) 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 GMT sample for TRP, NO_2 or NH_4 throughout the entire dataset, since this is when the instrument auto-calibrates.

There was no mains electricity at the Clatford site and therefore a propane-fuelled generator provided power for all the instrumentation and a three tubular heater controlled by a thermostat set to 20 °C. Fifteen minute flow data were supplied by the

EA, from a gauging station (Kennet at Marlborough, 39037) approximately 3 km downstream of the sampling location (Fig. 2). There are no major tributaries or sewage treatment work 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 Sigmatax 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. 3). 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 Sigmatax sampling probe were placed in this flow cell. The Sigmatax module is a sampling unit that draws the sample through a heated tube using vacuum suction. 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) and TRP (Hach-Lange, 2002). TP was determined colorimetrically on an acid persulphate 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 the phosphomolybdenum blue complexation (Murphy and Riley, 1962) . 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, respectively, for TDP and SRP, but the analysis is done on a filtered sample. This analysis was trialled at Bray 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. 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.

Fifteen minute flow data were supplied by the EA, from the gauging station (The Cut at Binfield, 39052) 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 Marina, the Bighams (Fig. 2), was also provided by the EA. 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, the system response was consistent and as such flow data from Binfield was used within this work as a surrogate for the flow at Bray.

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). NH_4 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 field. Samples for NO_2 and NO_3 were filtered (<0.45 µm) 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 at Bray.

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

Following temperature correction of the Brimpton high-frequency data, the high-frequency water quality data at both Brimpton and Bray show good agreement with the weekly manual samples analysed in the laboratory (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 NO_3 data resampled at different frequencies

A year of hourly NO_3 and TRP data, from December 2009 to December 2010, for the Brimpton monitoring station 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 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 GMT sample;
- weekly – the 09:00 GMT sample collected on a Monday;
- fortnightly – the 09:00 GMT sample collected every second Monday;
- monthly (1st) – the 09:00 GMT sample collected on the first day of the month;

- monthly (11th) – the 09:00 GMT sample collected on the eleventh day of the month; and
- monthly (21st) – the 09:00 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):

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

$$Q_r = \frac{\sum_{K=1}^{N} Q_K}{N} \tag{2}$$

where C_i is the instantaneous determinand concentration ($\mathrm{mg\,l^{-1}}$), Q_i is the instantaneous discharge ($\mathrm{m^3\,s^{-1}}$), and Q_r is the average discharge, based on higher frequency discharge records over that sampling duration. K is a constant which accounts for the duration of the record. Q_K is the recorded discharge at 15 min intervals.

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. Only measurements for the Enborne and The Cut are considered, given the problems on the Kennet (see Sect. 5.2) but it is useful to consider the monitoring at Clatford in terms of issues with the instrumentation to provide justification for the move to miniaturised sensor technologies. We examine the information about hydrochemical sources, processes and dynamics which would be missed by sampling at frequencies greater than one day. The suitability of deploying laboratory-based instrumentation into the field is discussed, given the experience gleaned in this study. Based upon our observation and experience, a case is then made for the need for novel, miniaturised field-based water quality sensors, specifically one based on ion chromatography.

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 were considered. The Enborne flow responds rapidly to rainfall events, varying over three orders of magnitude from 0.1 to 25.1 $m^3 s^{-1}$; 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 $m^3 s^{-1}$. However, The Cut still exhibits a rapid response to storm events due to the high proportion of urbanisation within the catchment. At Brimpton and Bray, during periods of low flow, a strong, two peak, flow pattern was identified each day. An example of this pattern is provided in Fig. 5. Although the two periods shown demonstrate a similar phase in the flow response within both catchments, with an early morning peak at approximately 05:00 GMT and an afternoon peak at approximately 17:00 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, then the timing of the double peaks will also vary (Palmer-Felgate et al., 2008; Withers and Jarvie, 2008). Although, the finding of a double peak in the flow each day was expected for The Cut, it was not anticipated in the Enborne, as this catchment is generally considered to be predominately rural. 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.

5.1.2 Dynamics in the TRP concentrations

The TRP concentrations ranged from 0.001 to 0.60 mg P l^{-1} and from 0.2 to 1.45 mg P l^{-1} on the Enborne and Cut, respectively. On The Cut, TRP and TP concentrations were strongly correlated with a relationship close to 1:1 (Eq. 3; 95 % confidence interval):

$$\text{TRP} = 0.99(\pm 0.0043) \cdot \text{TP} + 0.052(\pm 0.0025), \quad r^2 = 0.98, \quad (p < 0.01) \tag{3}$$

The high proportion of TP that is TRP suggests that P is being delivered to the system from sewage effluent discharges. Overall the TRP time-series for the 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. 6). 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 has shown that, under baseflow conditions, point sources, such as STWs and industrial effluents, are dominant as their constant delivery of P to the system 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). Under high flows, diffuse sources of P, from agricultural fertilisers and septic tanks, 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 TP and TRP measurements for the rural Enborne show that these explanations are based on emergent properties apparent in weekly and fortnightly datasets; sub-daily data reveal a far more complex, seemingly chaotic, system with subtle variations in dilution and concentration dependent on the antecedent conditions and bed suspension. The exhaustion of P supply from diffuse sources is also evident with the TRP concentration falling more rapidly than the receding limb of the hydrograph.

In the River Enborne, the preceding baseflow conditions in February 2011 were higher than in May 2011, indicating higher groundwater levels in February 2011 and a probable mobilisation of phosphorus from diffuse sources and septic tanks under high flow conditions (Fig. 6, left-hand column). Under the lower baseflow conditions in May, the point sources are dominant and there is an initial dilution of the TRP concentration with the first peak in flow, but a small mobilisation of phosphorus is evident as the TRP concentration increases in association with the second discharge peak most likely due to mobilisation of the stream bed (Fig. 6, right-hand column). 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. As in The Cut, the TRP concentrations also decline more rapidly than the receding hydrograph limb.

At both Brimpton and Bray strong diurnal cycling was evident in the TRP time series during low flow periods. In both catchments, the amplitude and phase of this cyclical pattern changed through the study period. A strong early morning peak with a secondary smaller peak in concentration in the mid to late afternoon was apparent at both Brimpton and Bray (Fig. 7). The presence of a two peak diurnal cycle, which strengthens when flow declines, is further indication of the STW dominance of P inputs within the two river-systems (Palmer-Felgate et al., 2008). This outcome highlights that, even within a predominantly rural catchment such as the Enborne, diurnal peaks in P concentration were evident due to inputs of final effluent from a small Sewage Treatment Works within the catchment. This finding contrasts with other work which attributed the instream SRP concentrations to diffuse contributions with subsequent in-channel processing (Evans and Johnes, 2004).

5.1.3 Dynamics in nitrate concentrations

The NO_3 concentrations measured in the Enborne ranged from 1.7 to 5.8 $\mathrm{mg\,N\,l^{-1}}$. The time-series showed a seasonal pattern with NO_3 concentrations initially increasing in the spring to reach an early summer maximum and then a decline through the autumn to reach a winter minimum. This pattern indicates a lack of dilution of point source inputs during the summer months. Streamwater NO_3 concentrations, measured in the Enborne, exhibited a weak negative relationship with flow ($r^2 = 0.19$; Fig. 8c). This weak relationship arose because of the compound effects of different process and pathways through the year when significant dilutions of NO_3 occurred at high flows, but also increases in NO_3 concentration were evident, for example in January 2010 (Fig. 8c). The dominant pattern of dilution is the opposite relation to that found in the River Lambourn, a nearby sub-catchment of the Kennet, were streamwater NO_3 concentrations were observed to increase with storm flow (Neal et al., 2004; Wade et al., 2006). The increase in nitrate concentration occurred because Chalk rivers are groundwater dominated and the groundwater NO_3 concentrations are high and more groundwater flows to the stream during high flow periods. The NO_3 signal in the Enborne was also dominated by a strong diurnal cycle which was strongest during the low flow periods of the spring and summer, reaching amplitudes of 0.6 $\mathrm{mg\,N\,l^{-1}}$, and a two peak diurnal phase was observed. Again, as with P, this two peak diurnal cycle most likely highlights the importance of STW discharges at low flows in a catchment considered "rural". The diurnal range is, at most, 0.5 $\mathrm{mg\,N\,l^{-1}}$ in an overall total of approximately 5 $\mathrm{mg\,N\,l^{-1}}$ namely, approximately 10 %. Nitrogen fixation and denitrification by the catchment and aquatic vegetation cannot be ruled out at this juncture (Bernal et al., 2005). The wooded margins of the Enborne are dominated by *Alnus glutinosa*, and N fixation is related to photosynthetic activity and is therefore greatest in the spring and summer when plant leaves are present. Maximum nitrogen fixation has been observed for *Alnus glutinosa* to occur at midday which corresponds in the most part to the diurnal peaks observed in the streamwater nitrate concentrations (Wheeler, 1971; Hoellein et al., 2009). 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 120 % 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 reduced plant growth during the winter months and hence less photosynthesis. Chlorophyll concentrations were also highest in the summer months, with concentrations of $93\,\mu g\,l^{-1}$ reached. Although, this is high, the concentrations were not as high as those recorded for major blooms in parts of lower Thames, which has a long residence time due to the large number of locks and weirs, and a large proportion of the primary productivity in The Cut is as 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 over the year and there are, at least, two alternative explanations for this. The first is that much of the respiration resulted from the decomposition of primary production, as opposed to microbial breakdown of organic material from STW final effluent (Palmer-Felgate et al., 2008). A second explanation is a seasonal effect, as solar radiation and air and water temperatures decrease so would photosynthesis and respiration, and this is the most likely of the two explanations. The result that the respiration and photosynthesis estimates both decline also suggests 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 Kennet where the TRP concentrations are lower than The Cut. There is no obvious link between the rate of photosynthesis and chlorophyll concentrations in The Cut and the rates of photosynthetic oxygen production are also higher than expected given the concentrations of chlorophyll present (Krause-Jensen and Sand-Jensen, 1998). This result is 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. 9). Thus, whilst there are numerous studies that show that weekly samples can be used to elucidate the seasonal and flow response of nutrients, the hourly data reveal a nuanced and 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 17:00–19:00 GMT followed by minimum saturation between 05:00–07:00 GMT (Fig. 10). The difference in saturation levels between these two points varied by 75 %, taking the system from under saturated at night to super saturated during the day. Similarly, TRP concentrations in the Enborne showed rapid decreases, between 05:00 and 12:00 GMT, greater than 100 µg P l^{-1} (Fig. 7b). 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 observed within the time-series, errors such as aliasing are introduced. It is well-known that sampling water chemistry on a weekly basis when the determinand is known to be driven by processes which vary on an hourly basis, such as solar radiation, means that although this high frequency component is still part of the measured concentration time-series, it cannot be interpreted as the time-series does not contain sufficient information. However, it should also be appreciated that the dynamics of a frequency greater than the sampling frequency which are captured may be incorrectly interpreted as noise, or potentially misinterpreted as a lower frequency behaviour (Siren and Vantsi, 2002; Harris and Heathwaite, 2005; G. Chen et al., 2006; Johnson et al., 2007; Halliday et al., 2012). This can be overcome to some extent using frequency filters (Kirchner, 2005).

To gain a true understanding of the hydrochemical dynamics, the sub-daily water quality data need to be used alongside on-going, long-term low-frequency (fortnightly) monitoring, experiments and manipulation studies to determine the key processes operating (Halliday et al., 2012) or filters need to be 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.

It is unlikely that the current generation of deterministic, process based models, like the INCA models, can reproduce these subtle variations in the N and P dynamics, observed in the sub-daily time series, with their present geometry and without having a large number of layers to represent stores to represent an exhaustion of sediment or nitrogen or phosphorus (Whitehead et al., 1998; Wade et al., 2002a, b). Even then, such models could not be applied to a river system with certainty due to the large number of parameters necessary, and current bucket-type models are known not to reproduce the fractal noise evident when streamwater concentrations are plotted in the frequency domain (Kirchner et al., 2000). Different approaches are proposed where models such as INCA can be used to estimate the annual mean concentrations based on land-use and deposition, the latter in upland areas with limited agriculture, and the seasonal patterns can be explained by land management and effluent dilution. The variability in the nutrient concentrations could then be characterised as noise using sub-daily measurements and superimposed on the annual and seasonal baseline. Thus the daily and sub-daily measurements would represent the natural variability of the river system nutrient concentrations. Deterministic model simulations could be run to identify how the baseline annual and seasonal patterns would change in response to environmental change scenarios and the variability characterised by measurement would represent the extremes around this new baseline. In this case an assumption would be made that the distribution of the extremes does not change and this represents our best guess until we have the data and process-understanding of how coupled macronutrient cycling will respond to environmental change. In addition, catchment-scale nutrient models must use a distribution of residence times to capture the pollutant transport (Kirchner et al., 2005).

5.3.1 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), help constrain process-based models (Jordan et al., 2007), and determine the processes operating (Palmer-Felgate et al., 2008). The results of this study show that resampling the hourly data from the Enborne at 7 and 24 h frequencies does not worsen annual load estimates of TRP and NO_3 compared to estimates based on daily sampling (Table 1). This was due to an exhaustion of material entering the river during storm events for phosphorus (Fig. 6). The reduction in streamwater nitrate to an asymptotic concentration at high flows, means that the nitrate concentration changes little in the River Enbourne in the higher flow range (10–25 $m^3 s^{-1}$) which means a daily concentration is representative of the hourly values in that 24 h period (Fig. 10c). 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, seven and 24 sampling frequencies, when the first and eleventh day in each month was used for the concentration estimate. This was a chance occurrence as re-sampling based on the 21st day each month gave annual loads 39 and 36 % different from those calculated using hourly sampling for TRP and NO_3, 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, not only for P, but for NO_3, NH_4 and NO_2 too and with accompanying measurements of turbidity, chlorophyll *a*, 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 at Bray, 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 resource was invested in identifying suitable sites 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 site 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 gauging station was 10 km upstream. Once installed, the instruments were visited each week for calibration and the collection of the 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, then 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 these rivers.

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 to part 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 fluorimeter 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 at Brimpton and Bray. 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 proved extremely difficult at Bray. 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., 2012a). 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 nitrate and ammonium. 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 the data provide early warnings of algal blooms (Palmer-Felgate et al., 2008; Lee et al., 2005). 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 and this is one of the causes of accuracy issues (YSI, 2007).

Overall the results show that the use of field-based laboratory instrumentation is highly beneficial but, based on the experiences of deploying and maintaining this equipment in this study, it is recommended that this is ultimately not 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 required 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.

5.5 The future of high frequency water quality monitoring

As discussed, intensive manual sampling programmes are impractical to sustain for prolonged time periods and the results of this monitoring programme have demonstrated that due to the restrictions of power availability and infrastructure and cost, the routine deployment of wet chemistry instrumentation into the field remains some way off. In addition to this, national and international networks of flow and water quality monitoring stations are declining as funding becomes increasingly limited and therefore there is a pressing need for reliable and cost-effective solutions (Stokstad, 1999;

Shiklomanov et al., 2002; Asante et al., 2008). Consequently, if high frequency hydrochemical monitoring is to become common place, 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; G. Chen et al., 2006; 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., 2002b; L. Chen et al., 2006). Most of the work on developing environmental methods for field applications has involved sensors or microfluidic devices for single analytes (Bowden et al., 2002a; Datta et al., 2007; Jokerst et al., 2012). However, as noted in this discussion, concentrations of a wide range of anions and cations are of interest. To measure a range of different species, it is necessary to initially separate them. Of the available techniques, ion chromatography with conductivity detection has proven to be one of the most versatile under laboratory conditions, and became extremely popular when Dionex introduced a commercial laboratory system in which a micro-membrane suppressor was utilised to give high sensitivity detection (Haddad and Jackson, 2003). Recently, miniaturised porous monolithic silica columns have been used for the separation of anions (Watanabe et al., 2009). Investigations using these phases have shown that very short columns can be used for low and medium pressure chromatography giving ultra-fast separations with comparable efficiencies (Victory et al., 2004). Ion chromatography can be achieved by modifying the surface with suitable reagents (Pearson et al., 2007).

As part of this ongoing project, we are attempting to create a novel system that will detect the range of ions that can be detected by ion chromatography on a chip; this could be as a miniaturised ion chromatography system or by using microchip electrophoresis (Fercher et al., 2010; Mahabadi et al., 2010). To achieve this miniaturised chemical analysis systems which use microfluidic devices, the so called “lab-on-a-chip” technology, are being developed and tested (Daykin and Haswell, 1995; Marle and Greenway, 2005). Whatever the method of ion separation, microfluidic systems have many advantages, including small sample and reagent volumes and a high degree of spatial (nm) and temporal (microseconds) control of processing, due to the diffusive mixing processes which are occurring within a laminar flow regime. Further advantages include the high surface to volume ratios which can be used to intensify liquid/surface, liquid/liquid or surface/surface interactions, and the capability to integrate complex processes with non-invasive analytical measurements in order to achieve better temporal and spatial resolution of dynamic processes than is currently possible with existing methodology. 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.

6 Conclusions

High frequency data provide significant benefits to understanding of catchment hydrochemical sources and behaviour. The sub-daily phosphorus and nitrate 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, then 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 the dominance of heterotrophic algae in controlling the photosynthesis and respiration dynamics. Daily data appear adequate for annual load estimation in these two catchments.

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 that 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 networks, deployable at remote locations.

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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 %	2.5 %
Monthly (11th)	3100	114 000	−7 %	−5 %
Monthly (21st)	2000	76 800	−39 %	−36 %

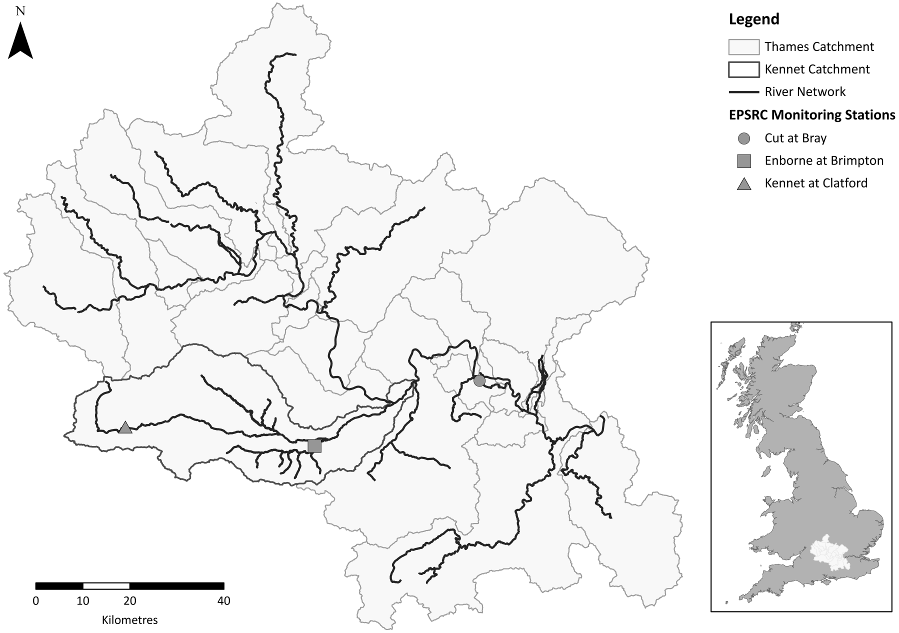

Fig. 1. Study site location map.

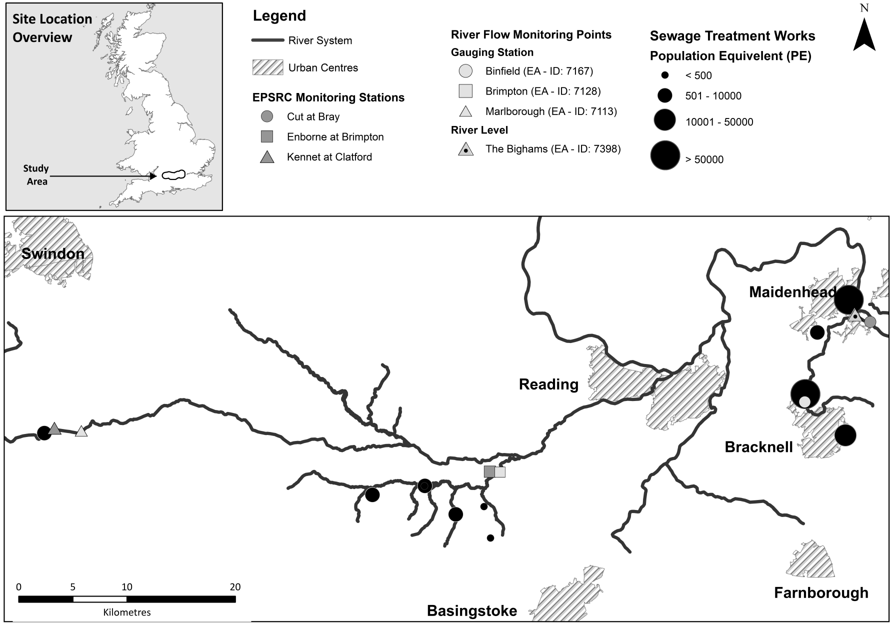

Fig. 2. Location of Sewage Treatment Works upstream of the river water quality monitoring sites.

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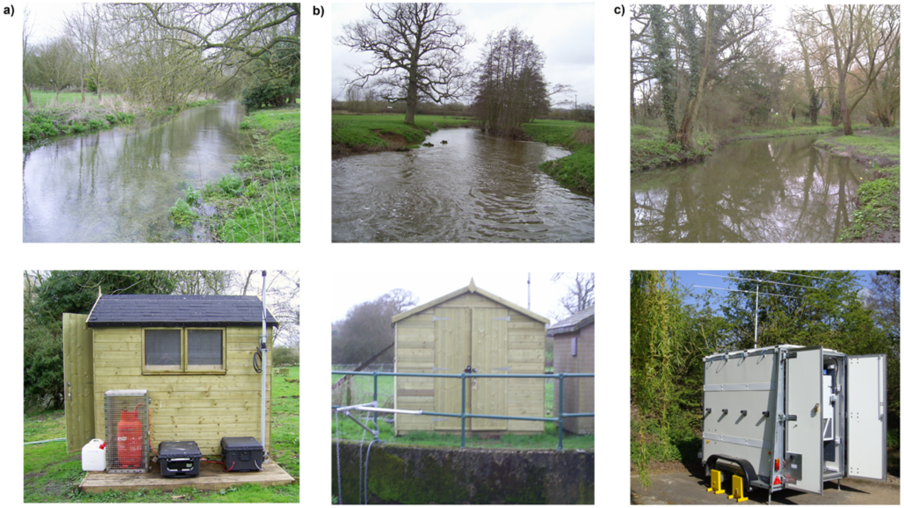

Fig. 3. Photographs of the river monitoring stations. River systems (top row: taken in March 2010): **(a)** River Kennet at Clatford (SU16016885), **(b)** River Enborne at Brimpton (SU56776477), and **(c)** The Cut at Bracknell (SU85837050). Monitoring stations (bottom row: taken in April 2010): **(a)**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

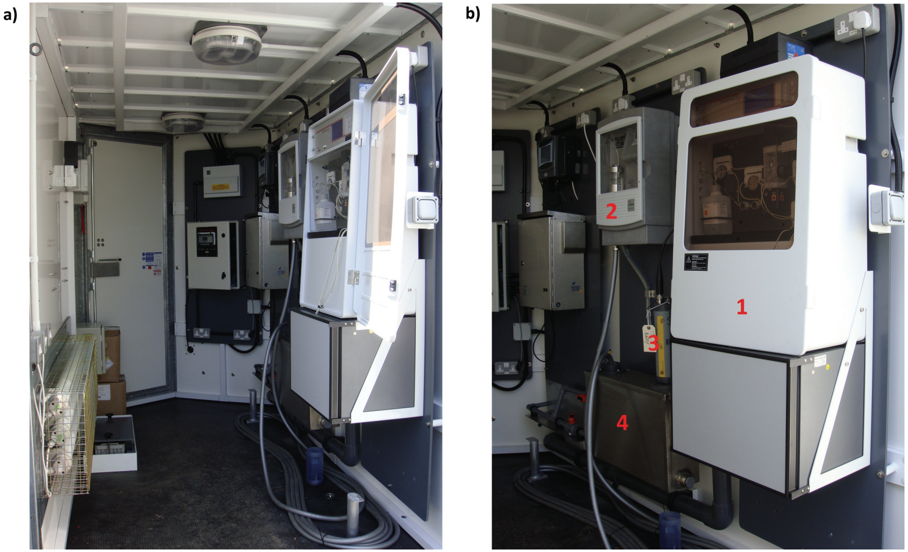

Fig. 4. An internal view of the monitoring station on The Cut taken on 22 April 2010 (SU91397866): **(a)** the layout of the station, with all monitoring equipment housed on the right-hand side and the heater on the left-hand side, and **(b)** close up of the monitoring equipment: (1) Hach Lange Phosphax, (2) Hach Lange Sigmtax, (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.

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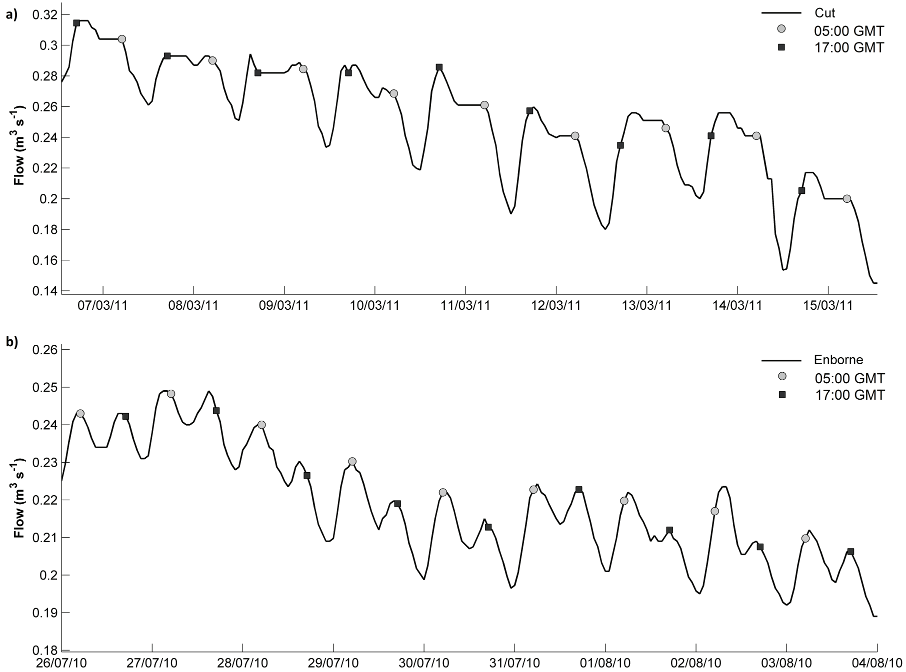

Fig. 5. Two peak diurnal pattern within the catchment flow time-series: **(a)** Binfield on The Cut; and **(b)** Brimpton on the Enborne. For the periods shown the two catchments are exhibiting a similar phasing in the flow diurnal cycle, with peak concentrations occur at either 05:00 or 17:00 GMT, followed in each case by a secondary peak 12 h later.

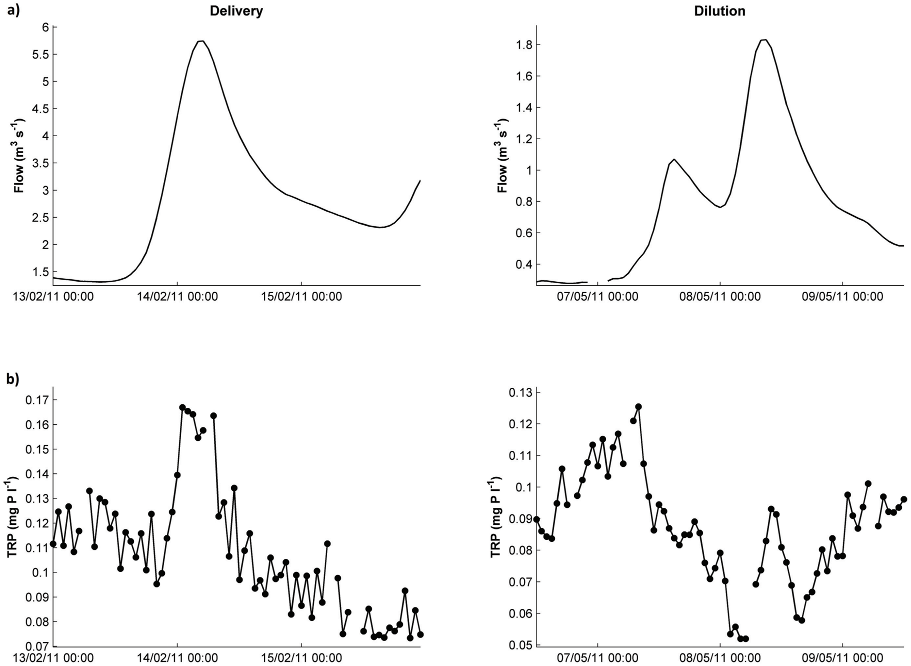

Fig. 6. Enborne TRP time-series demonstrating the changing relationship between TRP and Flow, with the left hand column showing a flow event delivering P to the system and the right hand column showing a flow event resulting in a dilution: **(a)** Flow ($m^3 s^{-1}$) and **(b)** TRP ($mg P l^{-1}$).

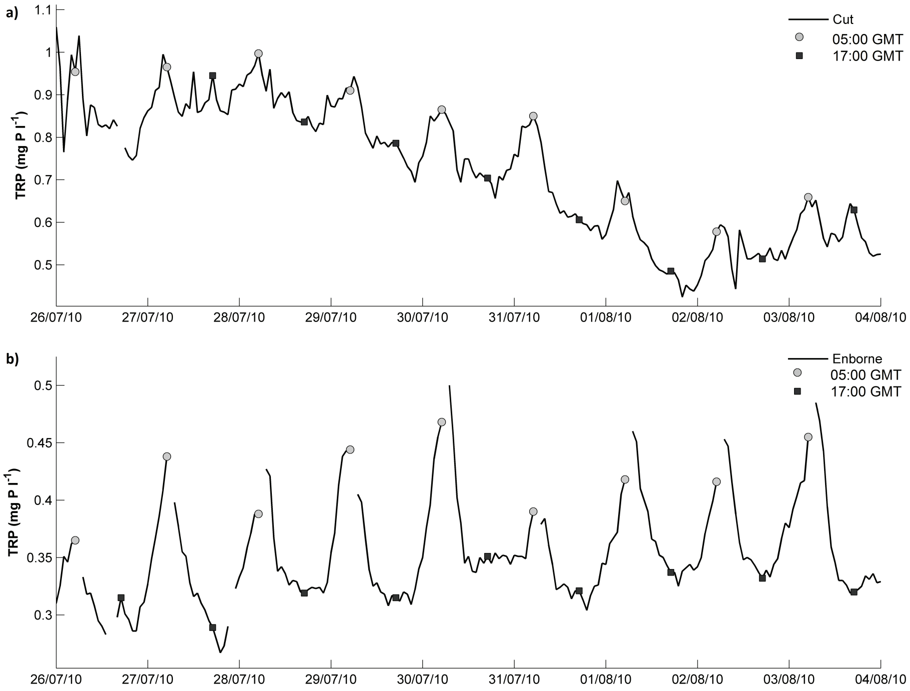

Fig. 7. Two peak diurnal patterns within the catchment TRP time-series: **(a)** the Cut and **(b)** the Enborne. For the period displayed peak concentration are occurring at approximately 05:00 GMT, with a small secondary peak occurring in the early afternoon on certain days. As discussed in the text, the Enborne system was auto-calibrating at 06:00 GMT, hence the data are always missing.

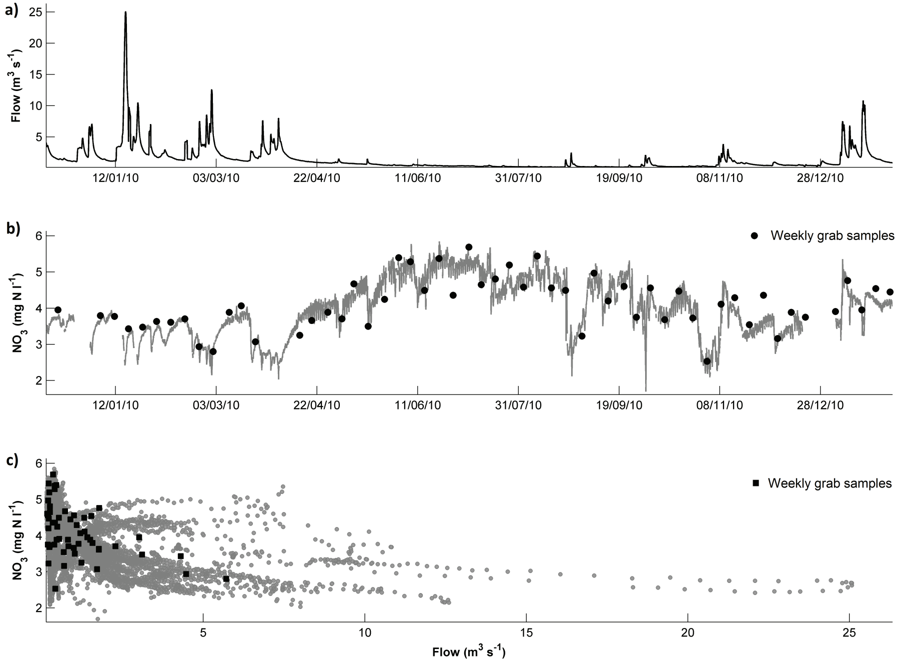

Fig. 8. Enborne nitrate time-series: **(a)** Flow (m^3 s^{-1}), **(b)** NO$_3$ (mg N l^{-1}) – dilution events are clearly visible during high flow events and **(c)** relationship plot of NO$_3$ against flow.

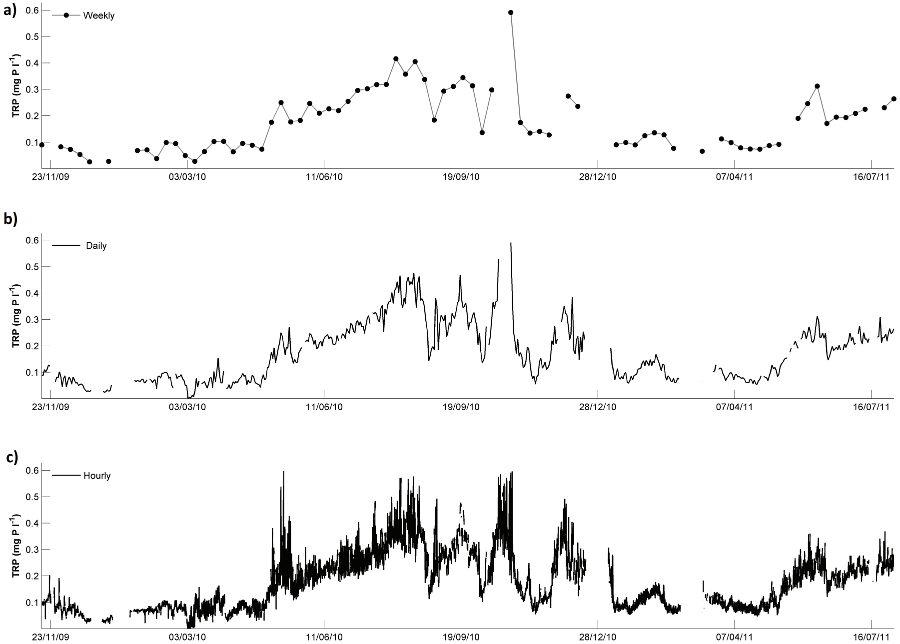

Fig. 9. Enborne TRP time-series: resampled onto lower frequencies to demonstrate the reduction information content as the sampling frequency decreases: **(a)** weekly, **(b)** daily and **(c)** hourly.

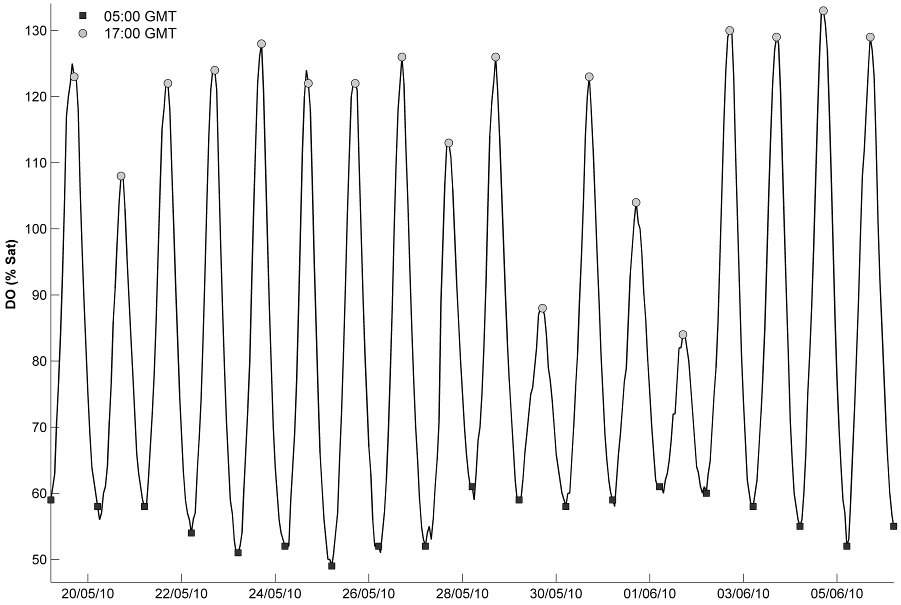

Fig. 10. Diurnal cycling within The Cut dissolved oxygen time-series, with peak saturation levels in the late afternoon, 17:00 GMT, and minimum saturation in the early morning, 05:00 GMT.