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High-frequency water quality monitoring in an urban catchment: hydrochemical dynamics, primary production and implications for the Water Framework Directive

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Abstract:

This paper describes the hydrochemistry of a lowland, urbanised river-system, The Cut in England, using *in situ* sub-daily sampling. The Cut receives effluent discharges from four major sewage treatment works serving around 190 000 people. These discharges consist largely of treated water, originally abstracted from the River Thames and returned via the water supply network, substantially increasing the natural flow. The hourly water quality data were supplemented by weekly manual sampling with laboratory analysis to check the hourly data and measure further determinands. Mean phosphorus and nitrate concentrations were very high, breaching standards set by EU legislation. Although 56% of the catchment area is agricultural, the hydrochemical dynamics were significantly impacted by effluent discharges which accounted for approximately 50% of the annual P catchment input loads and, on average, 59% of river flow at the monitoring point. Diurnal dissolved oxygen data demonstrated high in-stream productivity. From a comparison of high frequency and conventional monitoring data, it is inferred that much of the primary production was dominated by benthic algae, largely diatoms. Despite the high productivity and nutrient concentrations, the river water did not become anoxic, and major phytoplankton blooms were not observed. The strong diurnal and annual variation observed showed that assessments of water quality made under the Water Framework Directive (WFD) are sensitive to the time and season of sampling. It is recommended that specific sampling time windows be specified for each determinand, and that WFD targets should be applied in combination to help identify periods of greatest ecological risk. © 2015 The Authors. *Hydrological Processes* published by John Wiley & Sons Ltd.

KEY WORDS   The Cut; sewage treatment works; diurnal dynamics; instream productivity; phosphorus; Water Framework Directive

Received 25 July 2014; Accepted 28 January 2015

INTRODUCTION

With the development of new analytical equipment facilitating the collection of *in situ* sub-daily hydrochemical data the last decade has seen the expansion of high-frequency water quality monitoring schemes (e.g. Jordan *et al.*, 2005; Palmer-Felgate *et al.*, 2008; Rozemeijer *et al.*, 2010; Cassidy and Jordan, 2011; Bowes *et al.*, 2012a; Cohen *et al.*, 2012; Bieroza *et al.*, 2014). These new datasets have the potential to revolutionise our understanding of hydrochemical processes and reveal complex instream nutrient dynamics never before seen (e.g. Kirchner *et al.*, 2004; Heffernan

and Cohen, 2010; Macintosh *et al.*, 2011; Halliday *et al.*, 2013). To date existing studies have tended to focus on agricultural and rural catchments (e.g. Fealy *et al.*, 2010; Aubert *et al.*, 2013), with fewer published applications of deployments of *in situ* chemical analysers in urbanised river systems (e.g. Duan *et al.*, 2014; Viviano *et al.*, 2014). However, many river systems are affected by urbanisation. For example in the Thames catchment, southeast England, 70% of surface water bodies face significant pressure from point source discharges, 21% from water abstractions and 48% from flow regulation and morphological changes (European Commission, 2012). Water quality often diminishes along the rural to urban gradient as rivers become increasingly impacted and nutrient enrichment occurs. Globally the number of people living within urban areas is increasing year-on-year, with urban populations projected to account for 68%

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of the total global population by 2050 (United Nations, 2012). Within the UK, where urbanisation is already significant (79% of the population—49 million), it is anticipated that by 2050, 86% of the population will live in urban areas (63 million) (United Nations, 2012). Consequently it is critical that the impacts of urbanisation on water quality dynamics are fully evaluated.

In this study we expand high-frequency monitoring to an urban river, The Cut, which is situated in the Thames catchment, southeast England. The Cut provides an example of a small river which is impacted by urban discharges, water transfers between catchments and water abstraction. As population density increases, this will be an increasingly common situation in lowland England and other highly populated areas. Although modern sewage treatment prevents the gross organic pollution of the past, it is important to evaluate the effects of urban growth on water quality and compliance with legislative requirements, and to understand the hydrochemical functioning of such systems.

Specifically, in this paper, we evaluate the contribution that effluent discharges make to the hydrochemical dynamics of The Cut. The dominant sources of phosphorus in the river are identified using load apportionment modelling and an approximate system mass balance. The high-frequency instream hydrochemical dynamics are also assessed to determine how the system function was impacted by the catchment anthropogenic pressures outlined. The implications of these anthropogenic pressures for legislative water quality requirements are also reviewed. The impact of sampling frequency on the accuracy of legislative water quality assessment is evaluated, and recommendations are made about more appropriate monitoring strategies. Finally, there is discussion of how current legislative targets could be used to provide more insight into ecological risk.

CATCHMENT OVERVIEW

River morphometry and land use

The Cut rises from gravels to the south of Bracknell and flows northwards before joining the River Thames at Bray (Figure 1). It has been artificially diverted from its original course which was westwards to the River Loddon. Draining an area of approximately $124 \, km^2$, The Cut has three main tributaries: Bull Brook, Downmill Stream and the Maidenhead ditch. The monitoring station for streamwater chemistry was at Bray, approximately 200 m upstream of the river's confluence with the Thames (Figure 1).

The catchment geology is predominantly London Clay and Reading Beds (Palaeocene clays and sands), with deposits of gravel and alluvium as the catchment nears the

confluence with the River Thames (Environment Agency, EA, 2005). There are large areas of agricultural land within the catchment, with 30% designated as improved grassland and 26% as arable land, and there are significant areas of woodland, 15% (Figure 1) (Morton et al., 2011). The catchment also contains the large urban centre of Bracknell and part of Maidenhead.

Water resources

Public water supply within the catchment is affected by the Bray Water Pipeline Scheme (Figure 1). Under this scheme water abstracted from the River Thames and a gravel-borehole site at Bray, is treated at Bray Water Treatment Works and then pumped to storage reservoirs in Swinley Forest (Figure 1) (South East Water, 2007). From the reservoirs it is distributed to South East Water customers throughout the Northern Resource Zone, which includes Ascot, Bracknell and Maidenhead. The maximum consented abstraction rate is $95\,280 \, m^3 \, d^{-1}$, with an average abstraction of $63\,430 \, m^3 \, d^{-1}$. Water is then returned to the Thames via wastewater discharges. The Cut receives significant sewage treatment works (STW) discharges at Ascot (Population equivalent—25 500), Bracknell (97 500), White Waltham (6000) and Maidenhead (61 000), with an average total discharge rate of $51\,270 \, m^3 \, d^{-1}$ for all four works (Figure 1, Table I).

The Cut is gauged at Binfield, approximately 10 km upstream of the water quality monitoring site (Figure 1). The water quality monitoring site was not co-located at the gauging station because the monitoring equipment had to be housed in a secure location with mains power and this was not achievable at Binfield (Wade et al., 2012). At Binfield flow ranged from 0.06 to $5.4 \, m^3 \, s^{-1}$ during the study period and exhibited a rapid response to storm events because of urbanisation (Figure 2). The river's baseflow index at this point is 0.46 (Gustard et al., 1992; Marsh and Hannaford, 2008), significantly lower than the groundwater-fed rivers across much of the upper and mid-Thames basin.

Legislative designations

In the UK, legislative standards for river water quality are detailed under the EU Water Framework Directive (2000/60/EC). The aim of this legislation is that all water bodies achieve 'good ecological status' by 2015. WFD ecological status is determined by assessing a water body's biological, physicochemical, chemical and hydromorphological status, with the overall status determined by the worst scoring element. The majority of The Cut has been designated as a 'heavily modified water body' (HMWB), and has to achieve the alternative status 'good ecological potential' (EA, 2009). Water bodies are identified as HMWB when their physical
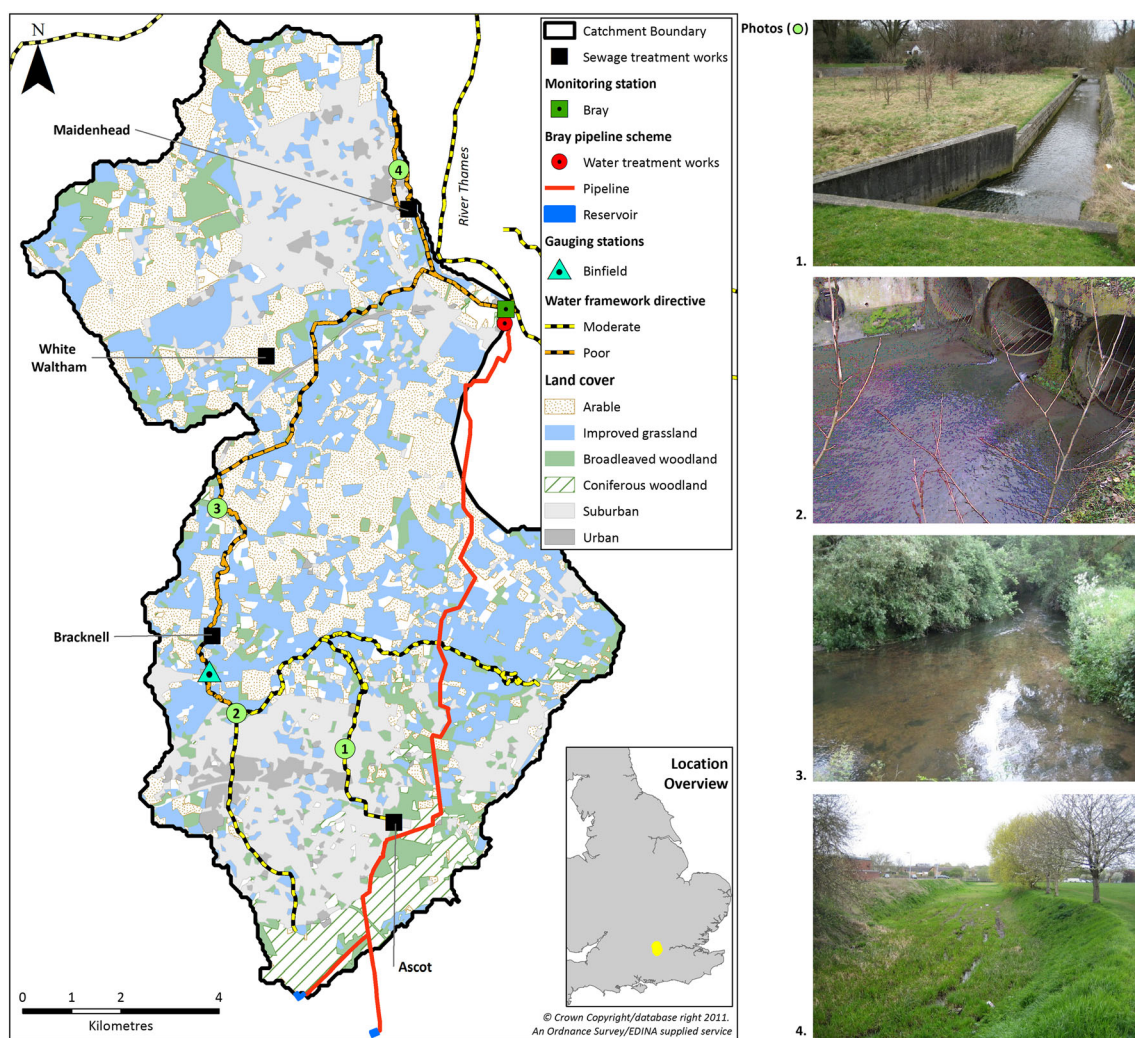
Figure 1. The Cut catchment: 1) Bull Brook 12/03/2009*, 2) Priestwood 01/04/2010, 3) Cox Green 11/09/2007*, 4) Maidenhead Ditch 25/04/2006*.
*Taken by Nigel Cox and licensed for reuse under a Creative Commons Licence

characteristics have been substantially changed and the hydromorphology changes necessary to achieve good ecological status would have a significant adverse impact on the water use (e.g. flood protection) or on the water environment. Good ecological potential is achieved when the hydromorphological characteristics have been improved to the fullest extent, without causing significant adverse impacts. To achieve 'good ecological potential' the water bodies still have to achieve the same biological, physicochemical and chemical targets specified for 'good ecological status', except where it is identified that the reason for element failure is hydromorphological, in which case the element can be excluded from the assessment (UKTAG, 2008).

At Bray, The Cut's ecological potential is currently classified as poor (Figure 1) (EA, 2009). This classification results from the 'poor' biological status, with the diatom ecological quality ratio (EQR) indicating that the river experiences a high level of pollution or disturbance (Poor: $0.26 \leq EQR < 0.52$). The current physicochemical status is 'moderate'. However, the river is yet to be assessed against the newly adopted phosphorus targets or the recently proposed pH and ammonia targets (Table II) (UKTAG, 2013a). The current chemical status is 'good'.

METHODS

Hydrochemical data

The high-frequency hydrochemical data were collected as part of the LIMPIDS Project and the monitoring methodology and data validation procedures are detailed in Wade *et al.* (2012). LIMPIDS was an exploratory project looking to test and evaluate *in situ* monitoring equipment across a range of sites with the Thames basin (Wade *et al.*, 2012). For this reason, the focus on The Cut

Table I. Information on the major sewage treatment works (STW) discharging to The Cut (Figure 1). Mean nutrient concentrations are provided based on available data from the Environment Agency (EA, 2012). Mean and maximum STW discharge % contribution to river flows were calculated using the mean daily discharge rates from the STW and the estimated mean daily flows at Bray[b] (Contains EA information © EA and database right)

	Ascot	Bracknell	White Waltham	Maidenhead
Population equivalent[a]	25 500	97 500	6000	61 000
Grid reference	SU890682	SU858718	SU865777	SU894807
Discharge point	Bullbrook	The Cut	Heywood Stream	Maidenhead Ditch
Distance from monitoring point (km)	15	10	5	3
Flow (2010–2012):				
Mean ($m^3 s^{-1}$)	0.08	0.23	0.03	0.25
Mean STW % contribution	8.0	22.6	2.8	26.2
Max STW % contribution	19.0	41.6	5.4	46.4
EA Data (2010–2012):				
0111: Ammonia ($mg N l^{-1}$)	0.13	0.52	2.26	0.14
0348: Phosphorus ($mg P l^{-1}$)	0.97	1.44	—	1.19
EA Data (2005–2008):				
Ammonium ($mg N l^{-1}$)	0.47	0.72	3.49	0.07
Total oxidised nitrogen ($mg N l^{-1}$)	23.7	28.4	25.4	7.81
Phosphate ($mg P l^{-1}$)	2.98	5.41	1.53	1.09

[a] Daily flow rates at Bray were estimated as described in the text.
[b] 1 PE is the biodegradable load in effluent discharge having a 5-day biochemical oxygen demand of $60 g O_2 day^{-1}$ (DEFRA, 2012).
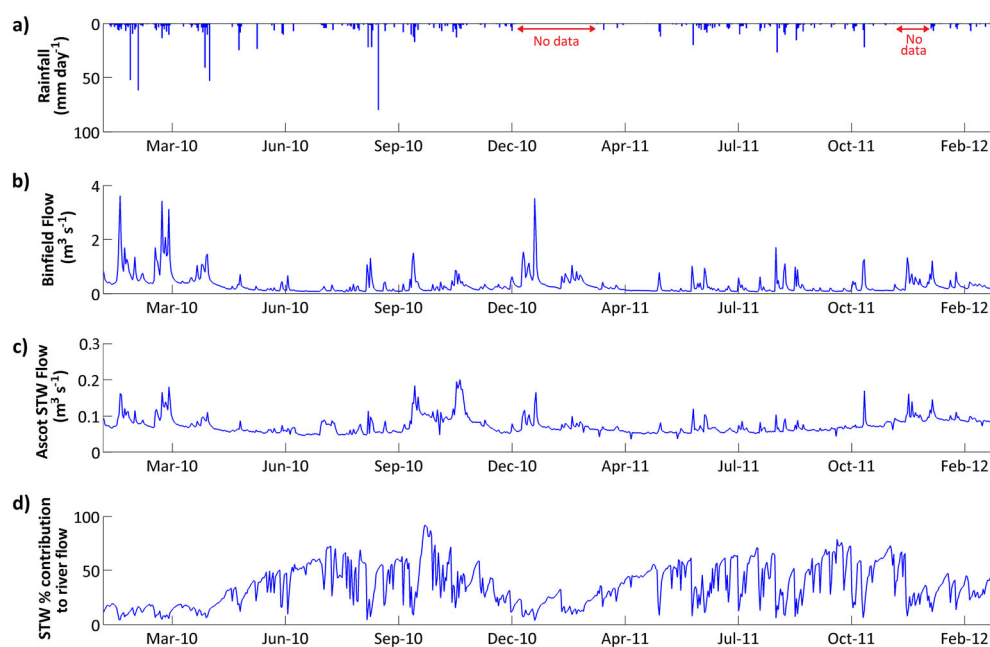— Data are not available.

Figure 2. The contribution that sewage effluent makes to The Cut flow at Binfield: a) Daily rainfall (Bracknell STW—MIDAS Weather Station—SRC ID 6165), b) Gauged mean daily flow at Binfield; c) Daily discharge rates from Ascot STW and d) The percentage contribution which effluent discharges make to the river flow at Binfield

was to assess the reliability of *in situ* instrumentation for collecting high-frequency phosphorus data within an urban effluent-affected system. Between April 2010 and February 2012, a YSI 6600 multi-parameter sonde measured conductivity, dissolved oxygen, pH, water temperature and turbidity and a Hach Lange Phosphax Sigma measured total phosphorus (TP) and total reactive phosphorus (TRP) on an hourly basis. The Phosphax Sigma determined phosphorus concentrations colorimetrically, TRP by phosphomolybdenum blue complexation (Murphy and Riley, 1962) and TP by acid persulphate digestion after heating to 140 °C, at a pressure of 2.5 bar (359 kPa) (Eisenreich *et al.*, 1975). There was no filtration step in either analysis. *In situ* sample filtration was

Table II. UK physicochemical Water Framework Directive targets applicable to The Cut (UKTAG, 2013a,b,c). Assessments are conducted on an annual basis and measures are based on the collected annual datasets

Determinand	Target	Measure	High	Good	Moderate	Poor
Phosphorus (mg P l^{-1})	Current	Mean reactive P	0.036	0.069	0.173	1.003
	Superseded	Mean soluble reactive P	0.050	0.120	0.250	1.000
Dissolved oxygen(% Sat.)	Current	10th percentile	70.0	60.0	54.0	45.0
Temperature (°C)	Current	98th percentile	20.0	23.0	28.0	30.0
Ammonia (mg N l^{-1})	*Proposed*	99th percentile	0.70	1.50	2.60	6.00
	Current	90th percentile	0.30	0.60	1.10	2.50
pH	*Proposed*	Mean	6.60	5.95	5.44	4.89
	Current	Percentile	5th ≥ 6.00		10th ≤ 4.70	10th ≤ 4.20
			95th ≤ 9.00			

trialled, however this proved unsuccessful and there are no *in situ* dissolved phosphorus measurements for this period (November 2010–January 2011) (Wade *et al.*, 2012). Power supply problems rendered the data between 13 March and 21 April 2011 unreliable. *In situ* monitoring was not undertaken for any nitrogen (N) species.

Throughout the monitoring programme, weekly 'grab-samples' were collected as part of CEH's Thames Initiative monitoring programme (Bowes *et al.*, 2012b), and analysed at the CEH laboratories in Wallingford for a wide range of chemical determinands. Samples were filtered in the field on collection and stored in the dark at 4 °C prior to analysis, which was undertaken within 48 h of sample collection. Complete sampling and analysis methodologies are given in the supplementary data accompanying Neal *et al.* (2012). Fifteen-minute flow data from Binfield gauging station (39052) were supplied by the Environment Agency (Figure 1).

Bray flow estimation

Mean daily flow rates at Bray were estimated as follows:

- The 'natural' river flow at Binfield was estimated using the recorded mean daily flow at Binfield minus the contribution from Ascot STW;
- This flow was then corrected for the increased catchment area at Bray (50 km^2 to 124 km^2); and then
- The mean daily discharge rates from Ascot, Bracknell, White Waltham and Maidenhead STW were added.

Stormwater discharges and water abstractions have not been included in the flow estimation as there were no available data.

Because of the complex nature of the catchment it is very difficult to accurately estimate or model sub-daily flow dynamics. The importance of STW discharges to the river's flow dynamics is evident even at Binfield with, on average, 36% of the observed river flow attributable to Ascot STW discharges (2010–2012: comparison of the daily mean river flows and STW discharge rates) (Figure 2). This contribution increased significantly during low flow periods when STW discharges could account for over 90% of the river flow (Figure 2). Analysis of the sub-daily flow dynamics at Binfield also demonstrated that at low flows a two-peak diurnal structure could be observed, resultant from the effluent discharge pattern associated with the STW (Figure 6a). Downstream of Binfield, The Cut receives discharges from three large STW (Figure 1, Table I), each of which has different (and varying) transit times to the monitoring site at Bray. As only daily discharge data are available for the STWs, it is not possible to model sub-daily dynamics at Bray with any credibility.

All subsequent analysis involving flow has been undertaken using the estimated daily flow rates at Bray and the measured mean daily hydrochemical concentrations. The diurnal flow dynamics at Binfield are presented only to demonstrate the importance of effluent discharges at this point on the river, and they are not compared directly with the diurnal hydrochemical dynamics at Bray.

Phosphorus mass balance and load apportionment

An approximate mass balance was performed for P to illustrate the relative importance of different nutrient sources. Annual input loads were estimated based on:

- Atmospheric P deposition rates, which are not measured routinely in the UK, based on recorded values at Frilsham (SU545731) (2002–2004) (Neal *et al.*, 2004);
- Fertiliser application rates, estimated from the Land Cover Mapping 2007 and the 2010 Agricultural Census data (Morton *et al.*, 2011; EDiNA, DEFRA, 2012); and
- Effluent discharge rates, estimated from reported STW flow and P concentration data (Table I), plus an estimated contribution from the unsewered population (calculated using an export coefficient approach, 0.54 kg P person^{-1} yr^{-1}).

Annual riverine output loads were calculated using the estimated daily flows and the recorded mean daily TP concentrations at Bray (Method 2—Littlewood, 1992. Because of data limitations, water abstractions, groundwater contributions and agricultural exports have not been considered.

The contribution of P from point and diffuse sources was also modelled using the Load Apportionment Method. This method is described in detail in Bowes *et al*. (2008), and only a brief overview is provided here. Calculations were made using the mean daily flow and P concentrations at Bray. The model assumes that the nutrient load from point, L_P, and diffuse, L_D, sources can be modelled as a power-law function of flow, Q, such that the total load, L_T at the sampling point is a linear combination of the contributions from both sources. Because the nutrient concentration, C_P, at a given sampling point is equal to the load divided by the flow rate, this can be expressed as Equation (2).

$$L_T = L_P + L_D = A.Q^B + C.Q^D \qquad (1)$$

$$C_p = A.Q^{B-1} + C.Q^{D-1} \qquad (2)$$

The parameters A, B, C and D are then empirically determined by imposing two constraints, based on assumptions about the behaviour of different nutrient sources with flow (e.g. Jarvie *et al*., 2006; Bowes *et al*., 2008; Halliday *et al*., 2014):

• Assuming point source inputs are continuous—increased flow can only reduce the P concentration: B < 1; and
• Assuming diffuse source inputs are runoff dependent—concentrations must increase with flow and tend towards zero at low flow: D > 1.

Evaluation of the in situ and laboratory analysis

The agreement between the *in situ* and laboratory measurements were assessed using a range of statistical measurements including: Pearson correlation coefficient, Nash–Sutcliffe efficiency criterion, *normalised* bias and *normalised unbiased* root mean squared difference (RMSD) (Jolliff *et al*., 2009) (Table III). The Pearson correlation coefficient measures the linear correlation between two measurements and the Nash–Sutcliffe criterion provides a measure of how well the *in situ* measurements can predict the laboratory measurements. The closer the statistics are to one the better the agreement between the two measurements. The bias provides a measure of the difference between the means of the two measurements and the *unbiased* RMSD represents the sample standard deviation of the differences between the

Table III. Goodness-of-fit statistics: h represents the high-frequency data; l the laboratory data; $\bar{h}$, $\bar{l}$, σ_h and σ_l are the respective dataset means and population standard deviations, and r is the Pearson correlation coefficient

Statistic	
Pearson correlation coefficient (r)	$\dfrac{\frac{1}{n}\sum_{i=1}^{n}\left(h_i-\bar{h}\right)\left(l_i-\bar{l}\right)}{\sigma_h\sigma_l}$
Nash–Sutcliffe efficiency criterion	$1-\dfrac{\sum_{i=1}^{n}\left(l_i-h_i\right)^2}{\sum_{i=1}^{n}\left(l_i-\bar{l}\right)^2}$
Normalised bias	$\dfrac{\left(\bar{h}-\bar{l}\right)}{\sigma_l}$
Normalised unbiased root mean squared difference	$\sqrt{1+\left(\frac{\sigma_h}{\sigma_l}\right)^2-2\left(\frac{\sigma_h}{\sigma_l}\right)r}$

two measurements. Both the bias and *unbiased* RMSD statistics have been normalised so the results for different determinands can be directly compared. For these statistics the closer the value is to zero the better the agreement between the two measurements (Jolliff *et al*., 2009).

Instream productivity analysis

The diurnal dissolved oxygen data was investigated to assess instream productivity and to identify the processes controlling the complex oxygen dynamics. Daily estimates of photosynthesis and respiration rates were made using the 'Extreme value method' which is based on the dissolved oxygen mass balance Equation (3) (Wang *et al*., 2003; Correa-González *et al*., 2014).

$$\frac{dC}{dt} = P(t) + K_a D - R \qquad (3)$$

Where $P(t)$ is the time dependent photosynthesis rate ($mg\,l^{-1}\,d^{-1}$); K_a is the reaeration rate coefficient (d^{-1}); D is the dissolved oxygen deficit calculated by $C_s - C$, where C is the dissolved oxygen concentration and C_s the saturation concentration at the given temperature ($mg\,l^{-1}$); and R is the respiration rate ($mg\,l^{-1}\,d^{-1}$).

Impact of sampling frequency

The impact of sampling frequency on the WFD status classification was explored by resampling the 2011 hourly dataset to create a series of datasets of coarser sampling frequency. These frequencies were selected to mimic more traditional water quality sampling regimes, under which sample collection would take place on a weekly to monthly basis and would be restricted to the working day, 0900 – 1700 GMT (e.g. Neal *et al*., 2004). The resampled time-series were as follows:

- Daily: 3 datasets consisting of samples collected at: 0900, 1200 and 1500 GMT. Representative times from the common sampling window employed in manual sampling schemes;
- Weekly: 9 datasets consisting of samples collected on: Monday, Wednesday and Saturday, at each of the three representative times;
- Fortnightly: 9 datasets based on the weekly resampling methodology but only incorporating every second week; and
- Monthly: 9 datasets consisting of samples collected on the first: Monday, Wednesday and Saturday, of the month respectively, at each of the three representative times.

RESULTS AND DISCUSSION

Comparison of in situ and laboratory instrumentation

A high degree of consistency was observed between the *in situ* and laboratory TP, TRP, temperature and conductivity measurements, with strong significant correlations, high efficiency scores and excellent agreement according to the Jolliff *et al.* (2009) criteria (Table IV and SI.1). As reported in other studies (Halliday *et al.*, 2014), the pH measurements did show differences, with the *in situ* measurements showing a positive bias compared to the laboratory measurements (Table IV and SI.1). Lower pH measurements in the laboratory analysis may result from sample deterioration prior to analysis, through processes such as ammonia degassing and nitrification. Despite these observations the average pH difference was small, <0.20 pH units across the measured pH range; therefore the *in situ* measurements have been used. The consistency between the comparable *in situ* and laboratory measurements is in agreement with other studies employing analytical instrumentation in the field,

and provides evidence that *in situ* chemical analysers, like the Phosphax, are a viable water quality monitoring option in rivers affected by urban discharges. However it should be noted that the expensive nature of this type of instrumentation and their high power supply requirements may still preclude their wide application (Wade *et al.*, 2012).

P catchment mass balance and load apportionment

Human effluent discharges accounted for a significant proportion (50.3%) of the annual P input loads to The Cut (Table V). Agricultural fertiliser inputs to arable land and grassland were also important, at 36.3% and 9.2%, respectively, with atmospheric P deposition minimal at 4.2% (Table V). Because of data limitations it has not been possible to quantify the importance of urban stormwater discharges to the annual catchment P loads. However as these discharges are sporadic they are unlikely to alter the dominance of effluent discharges to the annual P input loads, although they may be important for predicting specific pollution events.

These load calculations highlight that, although a significant proportion of the catchment is classified as

Table V. Phosphorus mass balance for The Cut catchment— 2010/11

System inputs	Estimated annual load (kg P yr^{-1})	Percentage of total load (%)
Atmospheric deposition	2640	4.2
Effluent discharges	31 800	50.3
Fertiliser: arable	23 000	36.3
Grassland	5840	9.2
Total	63 280	100
System outputs		
Riverine load	19 500	30.8

Table IV. Goodness of fit statistics between the laboratory measurements (Lab) and *in situ* high-frequency measurements (HF). Scatter plots of the comparable Lab and HF measurements are shown in SI.1, along with the target diagram which summarises the goodness of fit statistics according to Jolliff *et al.* (2009)

Statistic[a]		TRP	TP	Temp.	Cond.	pH
Mean	HF	0.60	0.64	12.0	942	7.74
	Lab	0.59	0.69	12.0	928	7.54
Standard deviation	HF	0.23	0.22	4.75	109	0.13
	Lab	0.30	0.32	4.37	114	0.12
No. measurements		43	44	68	56	66
Pearson's correlation coefficient [b]		0.94[***]	0.94[***]	0.98[***]	0.86[***]	0.26[*]
Nash–Sutcliffe		0.84	0.79	0.95	0.73	−3.52
Normalised bias		0.04	−0.17	0.01	0.11	1.70
Normalised unbiased root mean squared difference		0.40	0.42	0.23	0.51	1.28

[a] Total reactive phosphorus (TRP)—mg P l^{-1}; total phosphorus (TP)—mg P l^{-1}; temperature (Temp.)—°C; conductivity (Cond.)—µS cm^{-1}
[b] Correlation statistically significant at ***$p < 0.001$; ** $p < 0.01$; * $p < 0.05$

agricultural land (approximately 56%), the size of the STWs discharging to the river mean that they dominate the input loads to the river-system. Moreover, the majority of the agricultural P input will be retained by the crops or in the soil, whereas the sewage effluent is discharged directly to the river. The load apportionment modelling also supports this conclusion (Figure 3). Load apportionment modelling seeks to split the observed instream nutrient load into point and diffuse sources on the basis of the different relationships the sources exhibit with flow (Bowes *et al.*, 2008). The technique works under the assumption that point sources decline with increasing flow as they are a constant input, whereas diffuse sources increase with flow as they are runoff dependent. The results from The Cut indicate that only once flow rates have exceeded the 90th flow percentile ($4\,m^3\,s^{-1}$ at Bray) do diffuse source P contributions exceed point source P contributions (Figure 3).

Of the annual P loads input to the catchment it was estimated that 31% leaves the catchment in the river. As this estimation was based on daily mean flows and P concentrations, it is likely to be an underestimation of the true riverine load as the extremes in concentration dynamics experienced with flow have not been accounted for (Littlewood and Marsh, 2005). However, the output load is still considerably less than the STW inputs alone, suggesting that, at the present, P is being retained in the river. This instream retention of P is likely caused by biological assimilation, with potentially contributory effects of sorption and co-precipitation into the streambed sediment. The fact that such a high percentage of the inputs loads are being discharged by the river, 31% compared to only 4% observed in the Enborne, a neighbouring lowland river system (Halliday *et al.*, 2014), suggests that the P load being delivered to the system is far in excess of that required for biological assimilation by the aquatic organisms in The Cut.

Overview of water chemistry

Conductivity values on The Cut were high, with a mean value of $960\,\mu S\,cm^{-1}$ ($329–1877\,\mu S\,cm^{-1}$), resulting from high (mean concentration quoted):

- calcium (Ca), $99.8\,mg\,l^{-1}$, concentrations resulting from the calcareous groundwater and River Thames water—accounting for approximately 28% of the conductivity;
- sodium (Na), $67.4\,mg\,l^{-1}$, and chloride (Cl), $96.1\,mg\,l^{-1}$, concentrations resulting from road salt and water softeners, with a contribution from seasalt deposition—accounting for approximately 14 and 19% of the conductivity respectively; and
- NO_3, $14\,mg\,N\,l^{-1}$, and sulphate (SO_4), $28\,mg\,S\,l^{-1}$, concentrations as a result of STW discharges and atmospheric deposition—accounting for approximately 7 and 13% of the conductivity, respectively.

Phosphorus concentrations were also high, with a mean TRP concentration of $0.52\,mg\,P\,l^{-1}$ and maximum concentration of $1.75\,mg\,P\,l^{-1}$, suggesting the river is extremely hypertrophic (Durand *et al.*, 2011). No clear seasonal pattern could be observed in nitrogen species. However P concentrations were slightly higher in summer, with mean TRP concentration of $0.71\,mg\,P\,l^{-1}$ between June and August 2010 (Figure 4). This supports the conclusion that The Cut is point-source dominated, as nutrient concentrations are highest in the summer when river flows and dilution capacity are lowest. Seasonal nutrient dynamics may have been affected by the drought conditions experienced during the monitoring period, when average monthly rainfall volumes between March 2010 and February 2012 were 24% lower than the long-term monthly rainfall volumes. The high concentrations and summertime nutrient peaks suggest that the supply of nutrients is masking any uptake effect associated with instream biological processing. There was no obvious
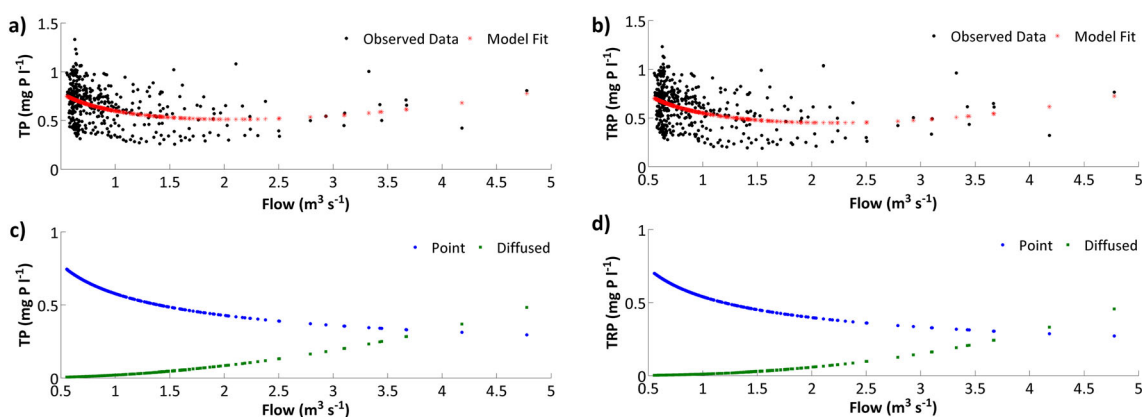

Figure 3. Relationship between flow and phosphorus fractions and the results of the load apportionment modelling. Top row shows the overall model fit and bottom row shows the modelled load apportionment split into point and diffuse sources: a, c) Total P ($mg\,P\,l^{-1}$) and b, d) Total reactive P ($mg\,P\,l^{-1}$)
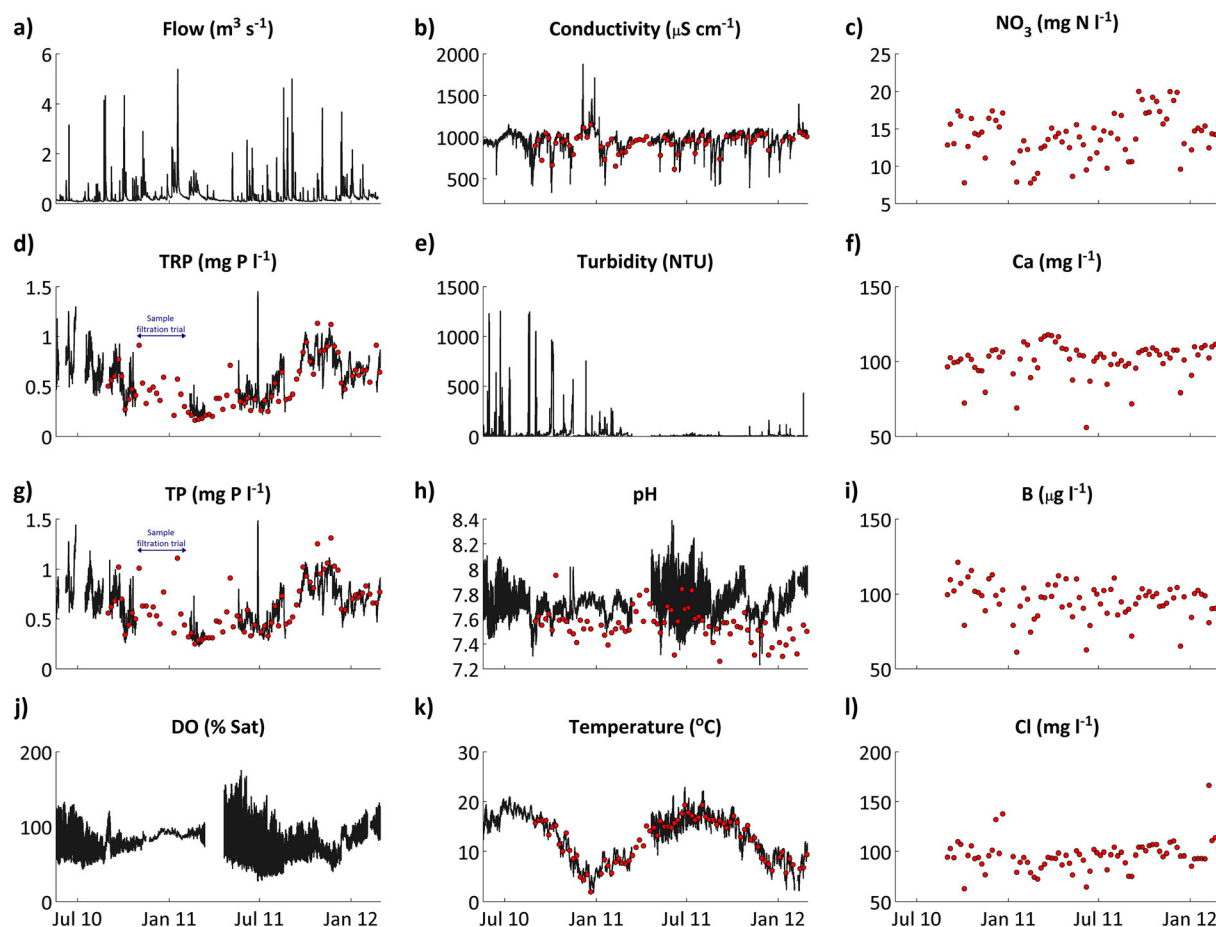
Figure 4. Time series of selected chemical determinands: a) Flow (15-min Binfield flow); b) conductivity; c) nitrate; d) total reactive phosphorus; e) turbidity; f) calcium; g) total phosphorus; h) pH; i) Boron; j) dissolved oxygen; k) temperature and l) chloride. The black lines are the *in situ* hourly data, and the red points the weekly Thames Initiative data

effect of fertiliser applications in the observed instream nutrient dynamics, with largely dilutions in nutrient concentration observed during high-flow events.

Nitrate was the dominant N species and soluble reactive P (SRP) the dominant P faction, accounting for on average 87% of the total dissolved nitrogen (TDN) and 78% of the total phosphorus (TP), respectively. Strong positive relationships were identified between TRP and TP (*in situ*) and SRP and TRP (weekly) (Figure 5). The high proportion of TP which is TRP, together with the high proportion of TRP which is SRP, is further evidence that the P being delivered to the system is from effluent discharges, with previous research demonstrating that soluble P fractions dominate effluent discharges (Jarvie *et al.*, 2006; Millier and Hooda, 2011). Under different flow conditions, differences in the TP and TRP relationship can be observed because of changes in the fractional composition of the TP. For high TP concentrations, observed largely under low flow conditions, nearly all the TP is TRP consistent with a STW origin (Figure 5c). However at lower TP concentrations, during

high flow events, some of the TP is comprised of other P fractions (Figure 5d). This P is most likely particulate P (PP) potentially from agricultural runoff, resuspended bed sediment or organically bound P including that in algal biomass (e.g. Jarvie *et al.*, 2006). This is supported by the observed increase in PP concentrations under stormflow conditions (flow > 90th flow percentile) (Table VI). The origin of PP in surface runoff is also supported by increases in dissolved organic carbon (DOC), iron (Fe) and aluminium (Al) concentrations under stormflow conditions, as these most likely originate in the soils of the catchment (Table VI).

Under baseflow conditions (flow < 10th flow percentile), concentrations of dissolved nutrient fractions increased, along with Na, Ca and boron (B) concentrations (Table VI). Higher Ca concentrations at baseflows can potentially indicate the increasing importance of calcareous groundwater inputs; however this not the driving mechanism on The Cut. As discussed, the catchment public water supply is provided by abstraction from the Thames or groundwater boreholes. This water
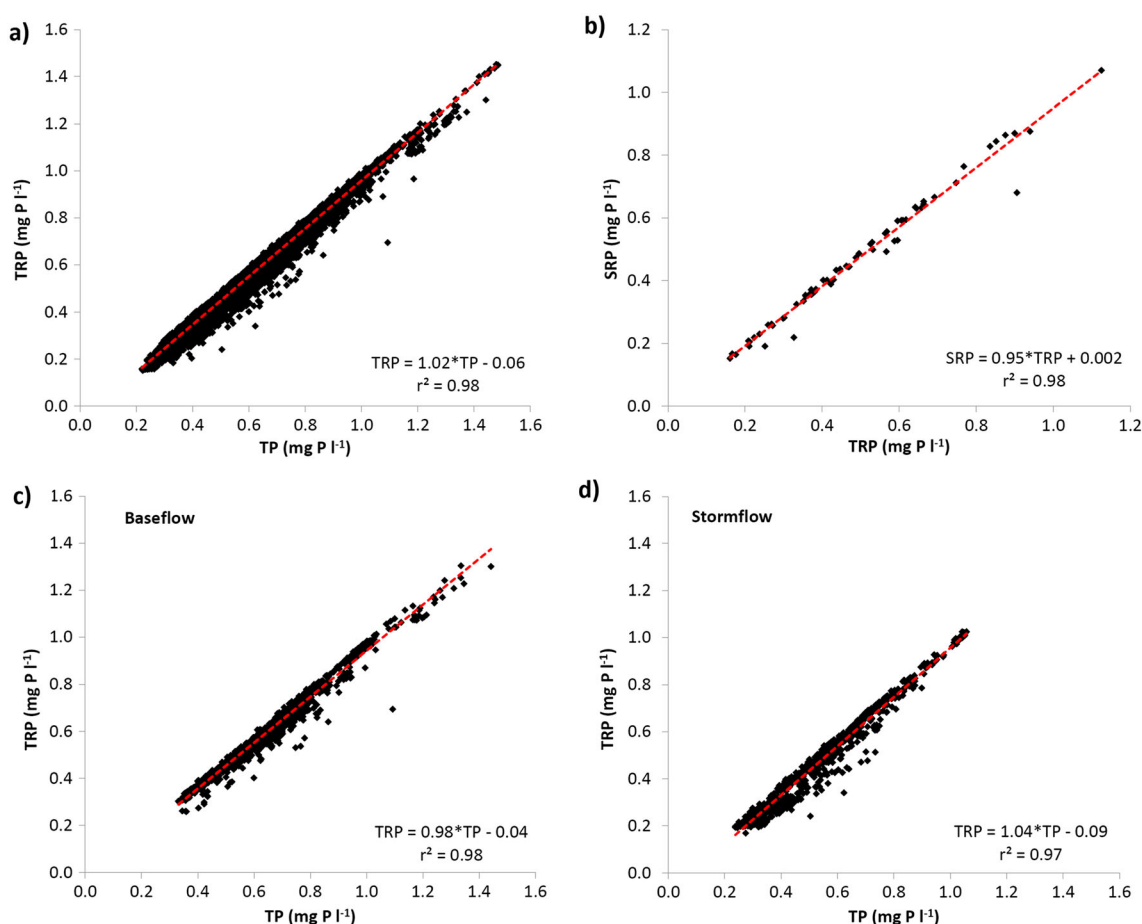
Figure 5. Phosphorus fraction relationships: a) total P (TP) *versus* total reactive P (TRP) (high-frequency); b) TRP *versus* soluble reactive P (SRP) (weekly); c) baseflow—TP *versus* TRP (flow < flow 10th percentile); and d) stormflow—TP *versus* TRP (flow > flow 90th percentile)

then re-enters the river through STW discharges, augmenting the natural flows. These abstracted waters, particularly from the groundwater boreholes, are likely to be enriched with Ca, relative to the natural waters in The Cut. As these waters travel through the water supply network they will become enriched with nutrients and contaminants associated with urban water usage. This is supported by the significant positive correlations Ca exhibited with B, a tracer for STW (Neal *et al.*, 2005; Rabiet *et al.*, 2006), and with TP, TRP, NO_3 and TDN (Table VII). Thus, the increase in Ca concentration at baseflows is further evidence of the dominance of effluent discharges in the system.

The impact of effluent discharges

STW discharges are exerting a significant influence on the river system at Bray with effluent discharges estimated to account for, on average, 59% of the river flow (based on the estimated Bray daily flow rates) (Table I). During periods of low flow, two-peak diurnal dynamics were evident in the hourly conductivity time series (Figure 6b),

and the P fractions also exhibited a strong diurnal cycles (Figure 6i, j). Regular two-peak diurnal dynamics have been observed in P in other lowland systems, such as the River Kennet, and attributed to the diurnal pattern in domestic water consumption (e.g. Palmer-Felgate *et al.*, 2008; Halliday *et al.*, 2014). The amplitude of the diurnal P dynamics on The Cut is comparable to the dynamics observed in other systems, with an average daily TP concentration change of $0.18\,\mathrm{mg\,P\,l^{-1}}$ at baseflows. However, the regular two-peak diurnal structure is not as evident on The Cut. This is likely caused by the different transit times of the effluent discharges from the four STWs to the monitoring location, resulting in the two peaks from each works being advected along the river system at different times. Hence the observed signal at Bray is more variable, with often a series of small daytime peaks overlaid on the larger diurnal pattern. In addition because the P concentrations are high, and a significant proportion of the river flow is derived from STW discharges, the concentration drop between the daily peaks is not as pronounced.

Daily variations in streamwater conductivity are normally associated with instream photosynthesis/respiration

Table VI. Water quality statistics for The Cut

	Units	Dataset[a]	Mean	Stormflow[b] Mean	Baseflow[b] Mean	Min	Max
Flow—Bray[c]	$m^3\,s^{-1}$	Daily	1.34	4.30	0.58	0.51	11.5
Flow—Binfield	$m^3\,s^{-1}$	15 min	0.26	0.99	0.08	0.06	5.39
Temp.	°C	TI	12.2	9.02	16.4	1.90	19.3
		HF	12.7	10.5	17.4	1.72	22.9
pH	n/a	TI	7.53	7.42	7.63	7.2	7.95
		HF	7.71	7.67	7.82	7.23	8.39
Cond.	$\mu S\,cm^{-1}$	TI	930	738	1000	613	1150
		HF	959	818	1010	329	1880
Turb.	NTU	HF	19.6	54.0	12.8	0.70	1260
DO	% Sat	HF	79.4	81.6	85.9	26.9	176
TP[d]	$mg\,P\,l^{-1}$	TI	0.66	0.64	0.71	0.25	1.81
		HF	0.65	0.53	0.66	0.22	1.49
TRP	$mg\,P\,l^{-1}$	TI	0.52	0.43	0.56	0.16	1.75
		HF	0.60	0.47	0.61	0.15	1.45
SRP	$mg\,P\,l^{-1}$	TI	0.52	0.41	0.58	0.15	1.74
TDP	$mg\,P\,l^{-1}$	TI	0.59	0.47	0.66	0.18	1.78
PP	$mg\,P\,l^{-1}$	TI	0.08	0.17	0.06	< 0.01	0.55
TDN	$mg\,N\,l^{-1}$	TI	15.3	11.3	17.5	5.36	23.1
NO_3	$mg\,N\,l^{-1}$	TI	14.0	10.8	15.6	7.74	20.0
NH_4	$mg\,N\,l^{-1}$	TI	0.15	0.20	0.08	0.01	1.30
DON	$mg\,N\,l^{-1}$	TI	1.89	1.72	2.24	0.13	4.77
DOC	$mg\,l^{-1}$	TI	7.42	10.3	6.18	4.40	21.2
Si	$mg\,l^{-1}$	TI	6.48	6.07	6.32	4.02	9.19
Na	$mg\,l^{-1}$	TI	67.4	53.9	75.3	29.0	106
Ca	$mg\,l^{-1}$	TI	99.8	80.6	103	54.7	118
Cl	$mg\,l^{-1}$	TI	96.1	88.2	100	62.9	166
SO_4	$mg\,S\,l^{-1}$	TI	27.6	26.5	27.0	17.9	34.1
B	$\mu g\,l^{-1}$	TI	93.3	74.9	101.0	55.3	121
Al	$\mu g\,l^{-1}$	TI	19.6	78.5	17.7	< 0.01	434
Fe	$\mu g\,l^{-1}$	TI	52.9	150	29.4	21.6	500

[a] HF = LIMPIDS high-frequency data, TI = CEH Thames initiative data.
[b] Stormflow: flow > 90th flow percentile; Baseflow: flow < 10th flow percentile (defined using 15-min Binfield flow record).
[c] Daily flow rates at Bray have been estimated as described in the text.
[d] Phosphorus abbreviations: TP, total P; TRP, total reactive P; PP, particulate P; TDP, total dissolved P; SRP, soluble reactive P.

dynamics (see section 'The impact of effluent discharges'). However the appearance of a two-peak cycle suggests that, on The Cut, STW discharges also drive diurnal changes in the streamwater hydrochemical composition. This is supported by the occurrence of a strong and regular two-peak diurnal cycle in conductivity in the winter when the diurnal cycling in dissolved oxygen is not evident (Figure 6). At this time daily variations in conductivity of between 25 and 35 $\mu S\,cm^{-1}$ are observed, with diurnal peaks occurring at approximately 0600 and 1800 GMT. In summer the more variable conductivity signal will be the composite signal resultant from the daily pattern in STW discharges, daytime declines driven by increasing photosynthesis rates and possible additional effects such as enhanced instream nitrification (see discussion of instream processing below) (Figure 6g).

Instream productivity

Despite the dominance of effluent discharges, The Cut never became anoxic, as observed in other urbanised systems (e.g. Harrison *et al.*, 2005), with dissolved oxygen concentrations ranging from a minimum of 27% to super saturated values of 176% (Figure 4). The dissolved oxygen dynamics were dominated by a strong diurnal cycle. The amplitude of diurnal dissolved oxygen fluctuations was strongest over spring and summer and displayed a classical cycle with peak saturation during the day (1500–1800 GMT), followed by minimum saturation at night (0300–0600 GMT) (Figure 7). Between April and June the dissolved oxygen level in the river reached saturation on a daily basis and minimum saturation levels remained almost constant (2010–60%; 2011–40%, Figure 7). Annual maxima in saturation were observed in mid April in 2010 (152%), and late May in 2011 (176%), with photosynthesis rates also peaking at this time (Table VIII). In late summer and early autumn the dissolved oxygen dynamics changed, with a significant decrease in the amplitude of the diurnal variability (Table VIII). In both 2010 and 2011, by mid-July, the system was failing to reach saturation consistently on a

Table VII. Spearman's rank correlation coefficients between the water quality parameters (correlation statistically significant at: *** $p < 0.001$; ** $p < 0.01$; * $p < 0.05$).

	Flow[a]	Temp[b]	pH[b]	Cond.[b]	Turb.[b]	DO[b]	TP[b]	TRP[b]	PP	TDN	NO$_3$	DON	DOC	Si	Ca	Cl
Temp[b]	−0.43***															
pH[b]	−0.29***	0.03**														
Cond.[b]	−0.44***	−0.06***	0.29***													
Turb.[b]	0.40***	−0.47***	−0.06***	−0.27***												
DO[b]	0.21***	−0.23***	0.67***	−0.06***	0.27***											
TP[b]	−0.33***	0.08***	0.06***	0.47***	−0.09***	−0.24***										
TRP[b]	−0.33***	0.05***	0.06***	0.48***	−0.10***	−0.23***	0.99***									
PP	0.32***	−0.57***	−0.35***	−0.04	0.46***	0.20	0.24*	0.07								
TDN	−0.55***	−0.08	0.22*	0.78***	−0.24	−0.02	0.4***	0.56***	−0.15							
NO$_3$	−0.54***	0.05	0.19	0.81***	−0.31*	−0.08	0.54***	0.59***	−0.16	0.95***						
DON	−0.14	−0.11	−0.34**	0.42**	−0.04	0.16	0.37**	0.33**	0.12	0.38***	0.51***					
DOC	0.33***	−0.24	−0.40**	0.40*	0.53***	−0.11	0.24	0.25	0.34*	−0.07	0.20	0.48***				
Si	−0.11	−0.27*	−0.14	0.53***	0.14	−0.24	0.26*	0.40***	−0.10	0.44***	0.54***	0.13	0.09			
Ca	−0.38***	−0.21*	0.33**	0.76***	−0.33**	0.35**	0.05	0.12	−0.07	0.55***	0.48***	0.26*	0.01	0.23*		
Cl	−0.40***	0.04	0.21	0.82***	−0.35***	0.01	0.51***	0.56***	−0.13	0.68***	0.74***	0.31***	0.04	0.39***	0.36***	
B	−0.53***	0.08	0.48***	0.58***	−0.18	−0.06	0.09	0.22*	−0.27*	0.61***	0.66***	−0.06	−0.03	0.47***	0.49***	0.46***

Notes:

[a] Flow-determinand relationships have been evaluated using the mean daily flow rates at Bray (estimated as described in the text) and mean daily determinand values.

[b] *In situ* hourly time series have been used; otherwise weekly Thames Initiative data have been utilised.

Temp. = Temperature; Cond. = Conductivity; Turb. = Turbidity; DO = Dissolved Oxygen; TP = Total Phosphorus; TRP = Total Reactive P; PP = Particulate P; TDN = Total Dissolved Nitrogen; DON = Dissolved Organic N; DOC = Dissolved Organic Carbon.
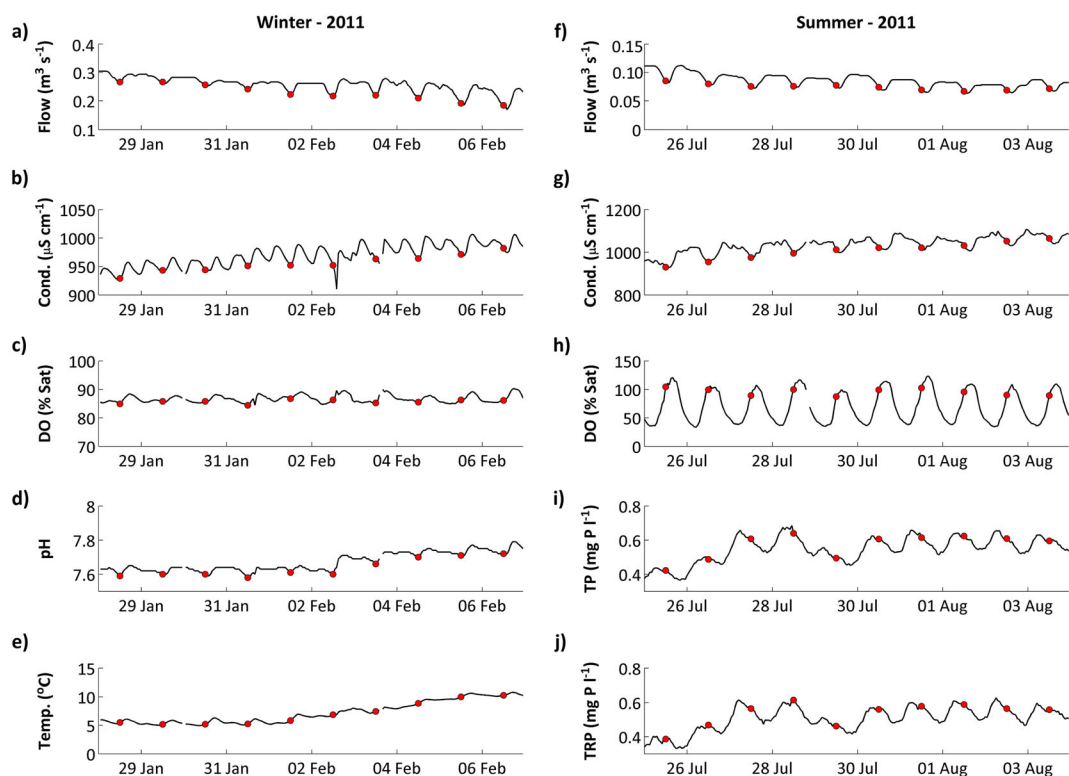
Figure 6. Extracts of the *in situ* high-frequency time series with the midday sample (1200 GMT) highlighted. The left-hand panel shows the 28 January–6 February 2011: a) flow (15-min Binfield flow), b) conductivity, c) dissolved oxygen, d) pH, and e) temperature. The right-hand panel shows the 25 July–3 August 2011: f) flow, g) conductivity, h) dissolved oxygen, i) total phosphorus and j) total reactive phosphorus
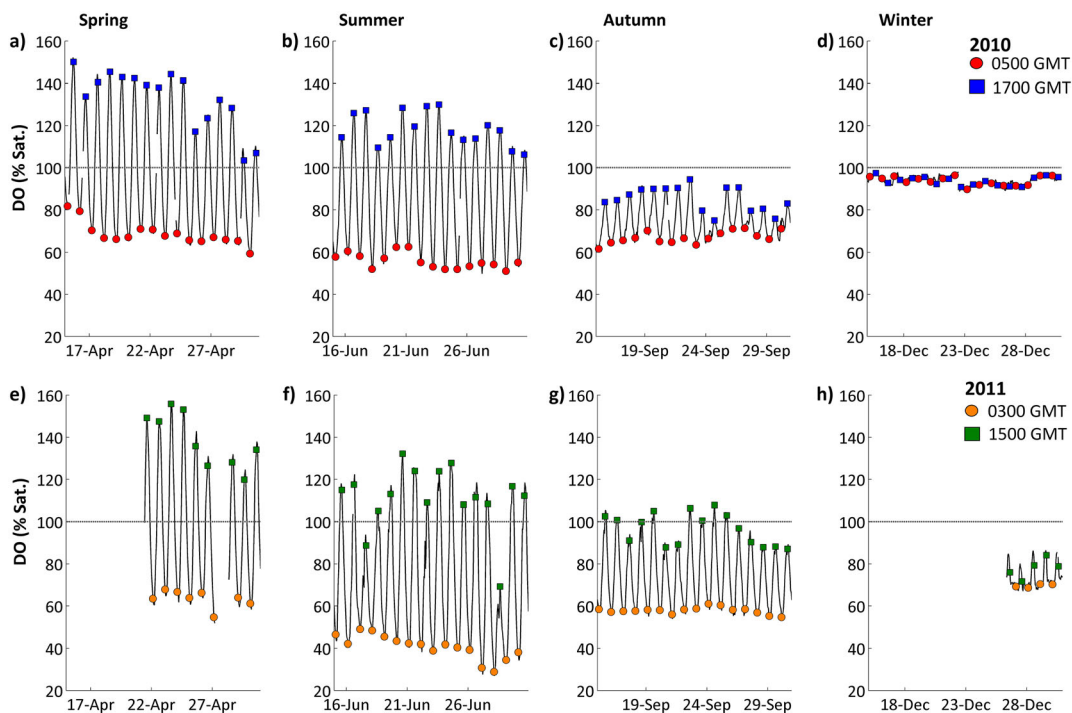

Figure 7. Dissolved oxygen dynamics. Plots show specific months: a), e) April; b), f) June; c), g) September; and d), h) December, with 2010 data on the top row and 2011 data on the bottom row. The 1700 and 0500 GMT and the 1500 and 0300 GMT sample times are highlighted for 2010 and 2011, respectively, to show the diurnal dissolved oxygen peaks and minimums

Table VIII. Determinand dynamics between the 15 and 30 days of each specified month (values reported to three significant figures)

		April		June		September		December	
		2010	2011	2010	2011	2010	2011	2010	2011
Flow ($m^3 s^{-1}$)	Mean	0.22	0.11	0.12	0.26	0.16	0.13	0.29	0.40
Dissolved oxygen(% Sat.)	Min	59.3	51.8	50.0	26.9	60.0	53.8	88.7	67.0
	Max	152	156	130	132	96.0	108	98.1	104
	Range[a]	66.9	71.0	64.4	74.8	20.4	41.9	4.28	16.0
Temperature (°C)	Min	9.79	11.8	13.9	13.4	12.3	12.7	1.72	4.40
	Max	15.5	18.0	20.6	22.9	16.8	19.0	7.49	10.8
	Range[a]	2.76	3.40	1.88	3.19	1.24	2.52	1.31	1.38
Solar radiation	Max	—	3120	—	3340	1900	1820	905	1010
	Range[a]	—	2690	—	2500	1290	1510	354	409
[b] P/R ratio	Mean	1.31	1.07	0.77	0.54	0.24	0.49	—	—
Respiration($mg l^{-1} day^{-1}$)	Mean	19.8	20.5	24.5	31.1	19.4	25.4	—	—
Photosynthesis($mg l^{-1} day^{-1}$)	Mean	25.3	21.1	18.7	17.4	4.66	12.3	—	—

[a] Average daily range.
[b] Daily estimates based on the extreme value method (Equation (3)).

daily basis and by mid-September the minimum daily dissolved oxygen saturation started to increase in comparison to the relatively steady baseline levels observed in late spring. By winter the dissolved oxygen diurnal cycle was completely absent, with only minor diurnal variability, and saturation was never reached (Figure 7).

In spring and early summer the instream dissolved oxygen diurnal cycle was driven predominantly by net photosynthesis. This is supported by a photosynthesis/respiration ratio (P/R) of > 1, indicating that autotrophic photosynthesis is exceeding heterotrophic respiration (Table VIII). If macrophyte photosynthesis was dominant, peak photosynthesis rates would not be expected until late summer, thus the occurrence of maximum dissolved oxygen saturation in late spring in both years suggests that this peak is being controlled by algal photosynthesis. This was supported by the occurrence of annual minima in silicon concentrations directly preceding the annual dissolved oxygen maxima, indicating the growth of diatom species. The lack of a discernible biological uptake signal in the nutrient dynamics suggests that nutrient availability is not a limiting factor in algal development, which is thus likely controlled by temperature and light. Major phytoplankton blooms were, however, not observed, with annual chlorophyll-a peaks of only $50 \mu g l^{-1}$, significantly lower than other systems studied in the Thames basin. The development of a major phytoplankton bloom was likely inhibited by the short river length, short water residence time and the artificial nature of the river flows (Bowes et al., 2012c). Flows are augmented through the water abstraction practices outlined, and are consequently higher than would naturally be expected. Thus water residence times are reduced, inhibiting the development of phytoplankton. However, the seasonal dynamics and high dissolved oxygen concentrations attained in spring suggest

that there is an algal bloom which must therefore be of benthic algae (periphyton).

The change in dissolved oxygen dynamics in the late summer and autumn indicates that net photosynthesis is no longer the dominant process. During this time the P/R < 1 and dissolved oxygen concentrations cease to reach saturation. This demonstrates that daytime photosynthesis, which has declined from springtime peak, is no longer sufficient to replenish oxygen levels following night time respiration, with respiration rates significantly higher than in spring (Table VIII). In other lowland systems dramatic reductions in dissolved oxygen diurnal dynamics in the late-spring/early-summer have been linked to the development of riparian shading, reducing light penetration to the stream and limiting photosynthesis (Hutchins et al., 2010; Halliday et al., 2014). On The Cut only 13% of the riparian corridor (defined as a 5-m strip either side of the river), is classified as deciduous woodland therefore although riparian shading may be a contributory factor in the reduced summer dissolved oxygen dynamics, is it unlikely to be the driving mechanism. Respiration results from the microbial breakdown of organic material from STW discharges and primary production, and will be enhanced in the summer by higher streamwater temperatures (Table VIII). Increased nitrification rates may also be exerting a greater influence on the oxygen dynamics at this time. Despite Ascot, Bracknell and Maidenhead STWs requiring tertiary treatment under the EU Urban Waste Water Directive (91/271/EEC), they still have significant final effluent N concentrations, with average ammonium (NH_4) concentrations between 0.07 and $3.49 \, mg \, N l^{-1}$ (Table I). Instream nitrification of these NH_4 discharges will contribute to the high streamwater NO_3 concentrations and higher summertime temperatures will increase

nitrification rates. This is supported by the higher NO_3 concentrations in summer, $17.2 \, mg \, N \, l^{-1}$, compared to spring, $12.9 \, mg \, N \, l^{-1}$. Nitrification can also be enhanced when heterotrophic assimilation of N is carbon limited (Trimmer *et al.*, 2012). The average $DOC:NO_3$ ratio in The Cut was 0.56:1, significantly below the ideal ratio for heterotrophic microbes of approximately 5:1.

In 2011, the diurnal oxygen dynamics did not decline as significantly as observed in 2010, with the levels still reaching saturation occasionally until mid October. Photosynthesis rates were significantly higher in autumn 2011 than in 2010 (Table VIII). This may result from continued algal growth, prompted by the lower flows and higher temperatures experienced in autumn 2011, associated with the 2011/12 drought.

The annual pattern in the instream dissolved oxygen dynamics of The Cut can thus be explained by the balance between seasonal changes in photosynthesis and respiration, with a possible contributory effect from nitrification. The importance of the benthic algae in driving the instream productivity has important implications for current monitoring practice. Most monitoring schemes, either *in situ* or grab-sample based, use stream chlorophyll concentrations as an indicator of instream algal dynamics (measured using fluorescence). However, these measures only account for algae suspended in the water column and do not account for benthic algae. Consequently, if instream productivity is to be fully evaluated in systems further work is needed to develop robust monitoring techniques that account for the wider contribution to net in-stream primary productivity from benthic and epiphytic algae, and macrophytes, as well as phytoplankton.

Water quality legislation

Nitrate concentrations on The Cut exceed the EU Drinking Water Directive (98/83/EC) standard, with 81% of the samples exceeding the $11.3 \, mg \, N \, l^{-1}$ target. The WFD physicochemical status attained for The Cut was 'poor', because although the status for pH and water temperature was 'high' the status for both P and dissolved oxygen was 'poor' (2011 hourly time series; Table IX). When new physicochemical criteria were being developed for the UK (UKTAG, 2013b), although not adopted, consideration was given to basing the physicochemical targets on the conditions during the 'growing period', defined in the WFD documentation as April to September inclusive. If this approach were adopted the physicochemical dissolved oxygen and temperature status both worsen, becoming 'bad' and 'good', respectively, thus resulting in an overall physicochemical status of 'bad'. The shift in system status with the variation in target specification suggests that further consideration needs to be given to the time of year when compliance sampling is done, as targeting measurements to a specific period of the year may provide a better indication of ecological vulnerability (see below). In addition, with such high nutrient concentrations it is questionable whether the nutrient targets stipulated under the physicochemical WFD guidelines are going to be achievable within heavily impacted systems like The Cut, especially given that P removal is already deployed at the three major STWs feeding the river (the UK requirement for tertiary P removal is that the STW must have a population equivalent greater than 10000 (DEFRA, 2012)).

Table IX. WFD status for The Cut under different sampling regimes. Only the results for the Monday re-sampled datasets are shown as the results were consistent for the Wednesday/Saturday datasets

Dataset	Hour (GMT)	Phosphorus	Dissolved Oxygen	pH	Temperature
Hourly	All	Poor	Poor	High/Good	High
	GP[a]		Bad		Good
Daily	0900	Poor	Moderate	High/Good	High
	1200		High		Good
	1500		Good		Good
Weekly	TI[b]	Poor	n/a	High/Good	High
	0900		Moderate		High
	1200		High		Good
	1500		High		Good
Fortnightly	0900	Poor	Moderate	High/Good	High
	1200		Good		Good
	1500		Good		Good
Monthly	0900	Poor	Good	High/Good	High
	1200		Good		Good
	1500		Good		Good

[a] Hourly data collected over the growing period.
[b] Weekly Thames Initiative data.

Impact of sampling regime. The sampling regime employed on the system did not affect the estimation of the WFD status of P, pH or water temperature. For pH and water temperature this was because 100% and 99% of the samples were in the 'high' WFD class, respectively (Figure 8). Similarly, because P concentrations were so high, a 'poor' status prevailed regardless of the sampling regime employed (Table IX). For dissolved oxygen the sampling regime significantly affected the WFD status. The diurnal variability of dissolved oxygen meant that under low-frequency sampling regimes, the WFD status

was sensitive to the time of day at which the sample was collected. For example, when the sampling frequency was reduced from hourly to daily, if samples were collected routinely at 0900 GMT then the WFD dissolved oxygen status attained was 'moderate', a one class improvement on the 'poor' status determined from the hourly data. However, if the samples were collected later in the day, the status determined from the daily datasets could improve to 'good' (1500 GMT) or even 'high' (1200 GMT) (Figure 8). By collecting samples in the afternoon, the regulatory agency may significantly over estimate the
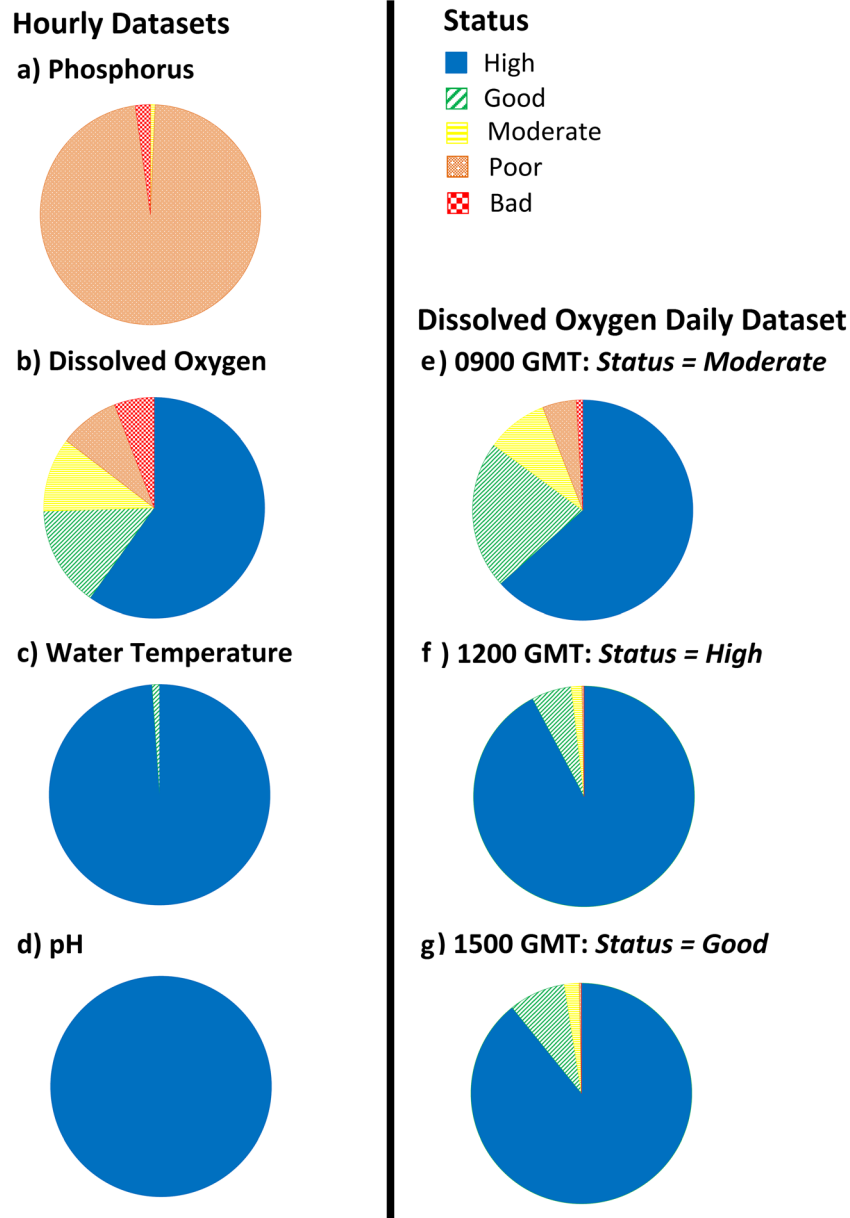

Figure 8. Water Framework Directive physicochemical classifications for The Cut based on the 2011 hourly determinand time series: a) phosphorus, b) dissolved oxygen, c) temperature and d) pH. Subplots e) to g) show the implications of sampling the system on a daily basis at specified sampling times for dissolved oxygen status determination

true 10th percentile of the annual dissolved oxygen time series. For WFD assessments to be accurate and consistent across catchments, it is recommended that specific sampling time windows be specified for each determinand. Implementation of this in the field will require a step change from the traditional sampling procedures adopted by regulatory agencies, in which samples are collected only during normal working hours (0900 – 1700) and sites are visited on a sampling route, which pays no attention to the sampling time at different sites. *In situ* multi-parameter sondes, which can be reliably used to measure determinands such as dissolved oxygen and pH, could provide a robust WFD monitoring solution, as sampling times can be directly specified at any time throughout the day or night and would not be restricted by the need for manual sample collection. This type of monitoring is already being implemented at a number of sites within England as part of the EA's catchment monitoring network (YSI and Loewenthal, 2008). For nutrients, such as TRP and NO$_3$, for which *in situ* monitoring technologies are still very expensive and pose significant operational challenges, setting a specific sampling window such as between 0800 and 1100 GMT

would be a first step in improving monitoring practices. The implementation of an agreed 'sampling window' would ensure that the analysis and assessment of the spatial and temporal nutrient dynamics would not be affected by artefacts introduced by differences in sampling time. Such an approach would also ensure consistency of assessment between different systems.

Ecological status assessment using multiple determinands. Little insight was gained into the ecological vulnerability of The Cut by reviewing nutrient concentrations against the WFD targets. As WFD targets are specified as annual means or percentiles, based on the spot samples collected by routine monitoring, there is no clear way for regulatory agencies to use the WFD targets to identify times of year when the system's ecological status is vulnerable. However it may be possible to identify periods of 'potential ecological risk' by combining WFD targets to highlight periods of particular ecological stress. For example, periods of 'potential ecological risk' could be defined as times when both P and dissolved oxygen concentrations breach the 'moderate' WFD thresholds. Other target combinations are possible, and this example
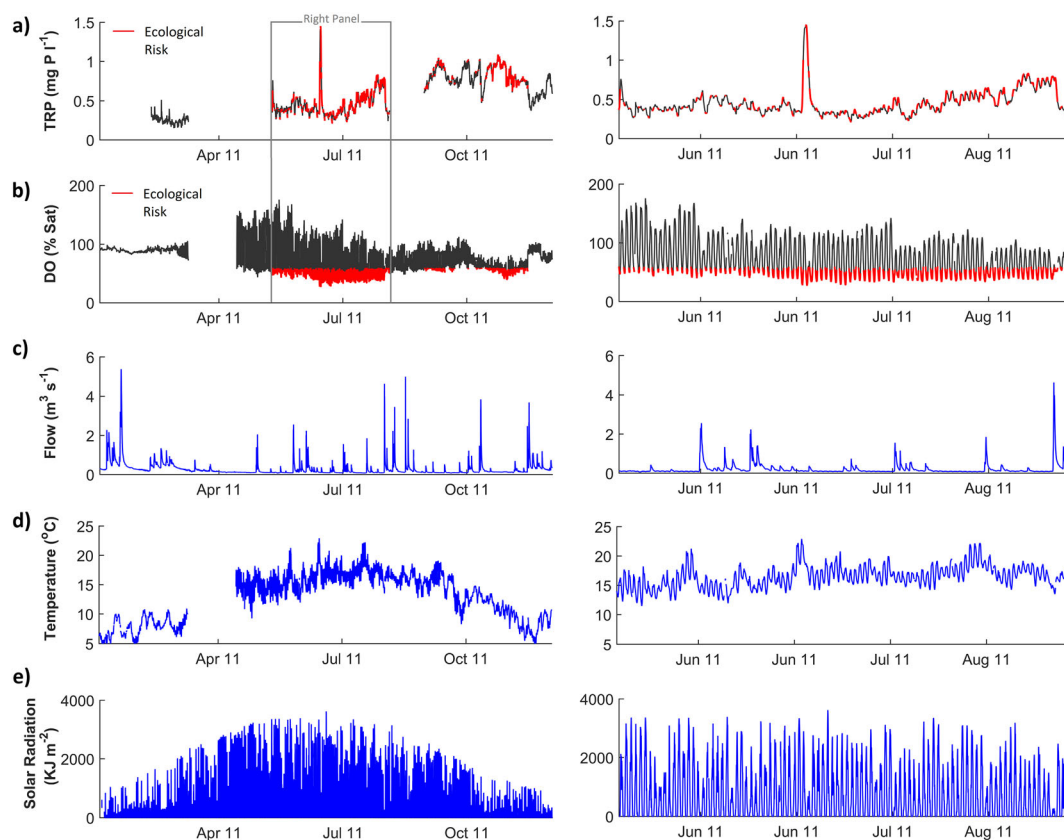

Figure 9. Periods of 'potential ecological risk' identified as times when both phosphorus and dissolved oxygen breach 'moderate' Water Framework Directive targets. The left-hand panel shows the entire 2011 time series, and the right-hand panel the constant period of risk identified between May and August: a) total reactive P; b) dissolved oxygen; c) flow (15-min Binfield flow); d) water temperature; and e) solar radiation (Eton Dorey MIDAS Weather Station SCR ID-56214)

simply provides an illustration of how this approach might work.

By considering P and dissolved oxygen in combination, a prolonged period of 'potential ecological risk' was identified on The Cut between 20 May and 22 August 2011 (Figure 9). At this time flows were low, $0.21 \, \text{m}^3 \, \text{s}^{-1}$; solar radiation values were high, $746 \, \text{KJ} \, \text{m}^{-2}$; and streamwater temperatures were high, $16.5 \, °C$ (mean values for this period). Together, these conditions place the ecology of the system under pressure as the high nutrient concentrations and low DO concentrations coincide with longer water residence times, high temperatures and high insolation, all factors likely to increase the potential for algal bloom development downstream in the River Thames. Over the May to August period, as a result of increasing periods of low dissolved oxygen concentrations the number of hours each day identified as times of 'potential ecological risk' increased from approximately 2 to 12 h. This may have important implications, for example, whilst fish and other aquatic fauna may cope with short periods of non-optimal conditions, sustained periods may increase the potential for negative ecological responses, such as fish kills. In addition, on rivers like The Cut there are limited refugia for fish, meaning that when system conditions worsen they are unable to temporarily relocate. By using the WFD targets in this way, regulatory agencies can target their monitoring practices and mitigation activities to periods when a system is most ecologically vulnerable. For example, the negative ecological impacts could be reduced by increasing the Thames abstraction rates during these times to help keep water residence times low in The Cut, or by placing stricter requirements on STW discharges (Bowes *et al.*, 2012a).

CONCLUSIONS

This study was one of the first to deploy *in situ* analytical instrumentation into a system heavily affected by urban discharges. The quality of the data reported have demonstrated that *in situ* chemical analysers, like the Phosphax, are capable of delivering good quality high-frequency hydrochemical data in these environments. In addition, the data derived from these technologies offer new insights into the chemical and ecological dynamics of a highly regulated and sewage impacted river, which would be unattainable from traditional low-frequency monitoring data.

The hydrochemical data revealed that the effluent discharges being received by The Cut exert significant influence on the water quality dynamics, with 50% of the annual P catchment loads attributed to effluent discharges. Diurnal hydrochemical dynamics also highlighted the dominance of effluent discharges, with the classical two-peak diurnal effluent discharge cycle observed in conductivity during the winter when other possible drivers, such as photosynthesis, have ceased. The P and N concentrations were extremely high breaching both the WFD 'moderate' threshold and the EU Drinking Waters limit, respectively. Despite these high nutrient concentrations and the lack of riparian shading, during the monitoring period no major phytoplankton blooms occurred and the river never became anoxic. We suggest that major phytoplankton blooms were prevented because the short river length and reduced water residence times, the latter resultant from the augmentation of river flow, did not allow sufficient time for bloom development. Further work is needed to look at the residence time of water in the system to fully quantify the effects of flow augmentation on instream algal dynamics. The importance of benthic algal growth to the instream productivity highlights the need for improved monitoring of this algal component.

The high nutrient loads to the river stimulate photosynthesis by benthic algae particularly, and this keeps the river well oxygenated during the day. Conversely, during the night, respiration predominates resulting in declining dissolved oxygen saturation but not to the point of anoxia. However, the situation is delicate with minimum dissolved oxygen saturations consistently below 50% in the summer. Any increase in organic loading, or other means to increase biochemical oxygen demand such as increased ammonia loading, at a period of low flow and high temperatures, may increase respiration and push the river into an anoxic state. The susceptibility of the system to changes in organic loading was demonstrated in June 2014, when a blocked pipe at Maidenhead STW resulted in only primary treatment effluent discharging directly to The Cut, causing anoxic conditions and fish deaths (Meechan, 2014). Any increase in river temperatures because of climate change (e.g. Bell *et al.*, 2012) might exacerbate the risk of anoxia by increasing respiration rates, especially at times when photosynthesis is light-limited.

This work has highlighted that the physicochemical targets specified under the WFD are likely to be unachievable in heavily impacted systems such as The Cut. The increasing pressure from predicted urban expansion is likely to mean that more river systems will face similar pressures to those experienced on The Cut, consequently reducing their ability to achieve the WFD targets. Sampling frequency and collection time had a significant impact on WFD assessments. For determinands which vary significantly on a daily basis the time of sample collection was critical, with the dissolved oxygen WFD class varying from 'poor' to 'high' dependent on the sampling time. Our findings

suggest that assessment of WFD physicochemical criteria which show a strong diurnal variability would benefit from identifying specific sampling time windows for each determinand. This would help make cross-comparison between sites and catchments more robust, and also facilitate more reliable evaluation of temporal patterns. Further work is recommended to develop WFD targets to identify periods when the river is most vulnerable to negative ecological impacts and thereby focus efforts on more targeted mitigation measures.

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article at the publisher's web-site. The data used in this study have been deposited with the CEH Environmental Information Data Centre (see http://www.ceh.ac.uk/data/), and will be freely accessible by searching for "The Cut". The database title is "Hourly physical and nutrient monitoring data for The Cut, Berkshire, 2009-2012".