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Article

The Water Quality of the River Enborne, UK: Observations from High-Frequency Monitoring in a Rural, Lowland River System

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Abstract: This paper reports the results of a 2-year study of water quality in the River Enborne, a rural river in lowland England. Concentrations of nitrogen and phosphorus species and other chemical determinands were monitored both at high-frequency (hourly), using automated *in situ* instrumentation, and by manual weekly sampling and laboratory analysis. The catchment land use is largely agricultural, with a population density of 123 persons km^{-2}. The river water is largely derived from calcareous groundwater, and there are high nitrogen and phosphorus concentrations. Agricultural fertiliser is the dominant source of annual loads of both nitrogen and phosphorus. However, the data show that sewage effluent discharges have a disproportionate effect on the river nitrogen and phosphorus dynamics. At least 38% of the catchment population use septic tank systems, but the effects are hard to quantify as only 6% are officially registered, and the characteristics of the others are unknown. Only 4% of the phosphorus input and 9% of the nitrogen input is exported from the catchment by the river, highlighting the importance of catchment process understanding in predicting nutrient concentrations. High-frequency monitoring will be a key to developing this vital process understanding.

Keywords: water chemistry; nitrogen; phosphorus; turbidity; conductivity; eutrophication; septic tanks; sewage treatment; high frequency; diurnal dynamics

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1. Introduction

The UK population is predicted to increase by 4.9 million people over the next decade [1]. This growth, along with increasing standards of living and continued economic development, is expected to be accompanied by an increase in water demand (e.g., [2,3]). With the anticipated background change in climate, it is expected that these social changes will place the UK's water environment under increasing pressure (e.g., [4,5]). This pressure will be particularly great in the southeast of England where population is predicted to increase the most, and water resources are already under strain as a consequence of low rainfall rates, high population density and high water usage rates [6,7]. Recent extremes in hydrological variability within the UK, ranging from the severe drought experienced during the summer of 2006 to the extreme flooding experienced in November 2009 [8–11], have emphasised the sensitivity of the UK's water resources to climatic fluctuations [4,8].

The UK's ability to meet the future demand for water in the face of increasing hydrological variability will depend not only on the quantity of water available but also on the quality. This has resulted in water quality issues becoming a major environmental concern (e.g., [12]). Water quality is governed in the EU by the Water Framework Directive (WFD: 2000/60/EC). The aim of the Directive is that by 2015, the ecological status of all designated water bodies within the UK should be classified as "good" (e.g., [13–17]). Good ecological status is achieved when the water body's biological community exhibits little departure from the natural community expected in such a water body [17]. Recent reports produced by the Environment Agency of England and Wales (EA), which is responsible for implementing the WFD, have recognised that many UK water bodies are at risk of failing to meet the target of "good ecological status" by 2015, with only 26% of rivers in England and Wales doing so in 2010 [7,18–20]. To improve the ecological status of river systems, it is necessary to understand the sources and processes directly controlling water quality and to quantify the impacts of anthropogenic pressures and climatic variability [21,22]. One of the recognised challenges is the ability to link catchment and within-river processes to specific in-stream water quality and ecological responses. The spatial distribution of nutrient sources and the role of a variety of processes in nutrient retention and remobilisation along the land-water continuum result in complex dynamics and lags in water quality responses, which make it difficult to deconvolute and apportion the dominant sources [13]. It is therefore difficult to develop appropriate management strategies and implement targeted mitigation measures when the sources and in-stream impacts of contaminants are not fully understood [13,23–25].

In southeast England, the major water quality problem is the high concentration of the major nutrients, nitrogen and phosphorus, in the region's rivers and groundwaters. Nutrient delivery to freshwater systems is traditionally split into two sources: "point" and "diffuse". Point sources such as industrial and sewage treatment works (STW) discharges provide a fairly constant, flow-independent delivery of nutrients to the system [26–28]. Diffuse sources such as atmospheric deposition and runoff from farmyards, fertilised fields and roads, are episodic and flow-dependent. There are also internal nutrient sources in the rivers such as nutrient-rich sediment and biota, which act as intermediate and temporary in-stream stores of nutrients derived from both point and diffuse sources [29–31]. In groundwater-dominated systems, historic contamination can also influence current water quality [32]. The importance of additional sources, such as septic tanks, sewage misconnections and combined sewer overflows on the water quality of river systems has also been highlighted in recent years (e.g., [33–35]). There is a lot of debate over whether nutrient releases from point or diffuse sources pose the greatest risk to streamwater quality (e.g., [14,36]). Recent research has highlighted that for water quality, and in particular the risk of eutrophication, the timing of nutrient releases to the system can be as critical as the volume of nutrients released [26].

The River Enborne, situated in Berkshire, southeast England, is a typical UK lowland river system, with a largely rural catchment. Water chemistry of the catchment was monitored between November 2009 and February 2012 using two protocols [37]. *In situ* instrumentation was used for high frequency (hourly) measurements of conductivity, dissolved oxygen, nitrate (NO_3), pH, total reactive phosphorus (TRP), turbidity and streamwater temperature. During this time, conventional weekly water quality samples were also collected and analysed in the laboratory for a wide range of hydrochemical determinands. This paper describes the Enborne catchment, quantifies the major nutrient inputs and outputs, compares the high-frequency and low-frequency datasets, and contains a preliminary analysis of the hydrochemical functioning of the catchment based on representative sub-sets of these data.

2. Methods

2.1. Hydrochemical Data

All data used in this paper are detailed in Table 1. The high frequency hydrochemical data were collected as part of the LIMPIDS Project [37]. The monitoring methodology employed in this project is outlined in detail in Wade *et al.* [38], along with the procedures employed for validating the data. Therefore only a brief outline of the instrumentation used and data generated is provided here. The *in situ* high-frequency water quality monitoring scheme commenced on 1 November 2009 and finished on the 29 February 2012. All instruments were deployed to make measurements on an hourly basis. A YSI 6600 multi-parameter sonde was used to measure conductivity, dissolved oxygen, pH, water temperature and turbidity [39]. The YSI sonde was calibrated every 2–3 weeks following standard operating procedures. A Systea Micromac C was used to make hourly measurements of total reactive phosphorus (TRP). The analysis method is based on the phosphomolybdenum blue complexation method and is undertaken on an unfiltered sample, hence TRP is an operationally defined measurement, predominantly comprised of orthophosphate (PO_4) and readily hydrolysable P species [38,40,41]. The instrument auto-calibrated daily at 0600 GMT, so there is no measurement for this hour within the dataset. Manual recalibration was undertaken fortnightly when the reagents were changed. A Hach-Lange Nitratax Plus probe was placed directly in the river and measured NO_3 using a reagent-free, ultra-violet (UV) absorption technique [38,42].

Table 1. Sources of data for this paper.

Determinand	Site	Location	Frequency	Duration	Start	End
Flow	Brimpton Gauging Station—39025	SU567647	15 min	46 years	1967	Ongoing
Water quality	Brimpton	SU567647	Hourly + Weekly	2.3 years	9 November	12 February
Rainfall volume	Kingsclere STW	SU530609	Daily	32 years	1981	Ongoing
Air temperature	University of Reading	SU739719	Daily	45 years	1968	Ongoing
Agricultural Census Data	Enborne catchment	2 × 2 km grid squares	Annual	1 year	2010	-
Atmospheric N Deposition	Enborne catchment	5 × 5 km grid squares	Annual- modelled	3 years	2009	2011
Atmospheric P Deposition	Frilsham	SU547734	Weekly	2 years	2002	2004

Throughout the monitoring programme, weekly "grab-samples" were collected at the Brimpton site, as part of the LIMPIDS ground-truthing scheme [38] and CEH's Thames Initiative monitoring [43] and analysed at the CEH laboratories in Wallingford for a wide range of chemical determinands including major ions, nutrients, trace elements, pH, alkalinity and conductivity [38,44]. These methodologies are outlined in the supplementary data accompanying Neal *et al.*, [45]. Fifteen- minute flow data were supplied by the EA from the Brimpton gauging station (39025), which is located immediately adjacent to the Enborne water quality sampling location (Figure 1a).

2.2. Catchment Description and Mass Balance

Population data were obtained from the latest UK Census, conducted on 27 March 2011. The data were extracted at a parish or smaller area level from the "Neighbourhood Statistics" census record for "usually resident population" (*i.e.*, including students and others normally resident in the Parish, even though living away on the census date) and number of households [46]. Conveniently, parish boundaries coincided with about 65% of the topographic catchment boundary. Where the boundaries did not coincide was mostly along the south side of the catchment in areas of low population density. In these cases an adjustment was made by counting houses visible on satellite imagery. The resident population figure is thus believed to be reasonably accurate.

Information on the agricultural practices within the catchment were obtained from AgCensus data for 2010 [47], and the CEH Land Cover 2007 map (LCM2007) [48]. Data from the British Fertiliser Practice Survey of 2010 and 2011 were used to estimate the amount of fertiliser used within the catchment, based on the identified crops grown (Table 2) [49]. The estimated areas of these crops were multiplied by these rates to obtain overall fertiliser inputs.

Table 2. Average overall nitrogen and phosphate fertiliser use in the UK between 2010 and 2011 (kg ha^{-1} yr^{-1}) [49].

Land Use Type	Total Nitrogen (N)	Total Phosphate (as P)
Tillage Crops	146	13
Grass	60	4
All Crops and Grass	100	8

Annual estimates of total atmospheric N deposition were obtained from Department for Environment, Food and Rural Affairs (Defra) [50], and for atmospheric P deposition (not measured routinely in the UK) values from Frilsham, 8 km north of Brimpton, measured in 2002–2004 were used [51]. Catchment rainfall data were based on measurements from the weather station at the Kingsclere STW (SCR ID 6024), located 5 km from the Brimpton monitoring point [52]. The nearest weather station recording air temperature was located outside of the catchment, on the University of Reading Whiteknights campus (SCR ID 830) 18 km from the Brimpton monitoring point. Data on the location and population equivalents (PE) of STW were obtained from official sources [53]. The PE is the unit of measure used to describe the size of a STW discharge, where 1 PE is the biodegradable load in STW discharge having a 5-day biochemical oxygen demand of 60 g of oxygen per day [54]. Loads from STWs were calculated using discharge data and monitored concentrations from the three largest works (Table 3) and adding a proportion representing the output from the smaller works, as these were not sampled frequently enough to give accurate direct estimates (Table 3). Loads from septic tanks were estimated as follows. The sum of the PEs of the documented STWs is 11,360. The catchment population estimate was 18,260, meaning the unsewered population is at least 6900, or 38%. This is almost certainly an underestimate as some of the PE of the STWs will not relate to the domestic population, but is consistent with other studies in similar catchments. The census shows there are an average of 2.5 persons per household, so this equates to a total of 2760 septic tanks. A septic tank is a small domestic sewage treatment system, consisting of a tank with a retention time of a few days which normally discharges to a shallow soil soakaway, though some tanks discharge directly to a watercourse. There are 163 registered household discharges, hence the number of unregistered septic tanks is approximately 2600 or 94% of the total. To estimate loads from septic tanks, an export coefficient approach was adopted, using values of 0.54 kg P person^{-1} yr^{-1} and 2.5 kg N person^{-1} yr^{-1} [35].

Annual nutrient export in the River Enborne was calculated using a standard flux-based algorithm based on metrics of instantaneous discharge and concentration [55–57]:

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

$$Q_r = \frac{\sum_{k=1}^{n}Q_k}{N} \tag{2}$$

where L_E is the estimated load (kg yr^{-1}); K is a constant which accounts for the duration of the record; C_i is the instantaneous determinand concentration (mg L^{-1}); Q_i is the instantaneous discharge (m^3 s^{-1}); and Q_r is the average discharge, computed as described in the second equation; where Q_k is the recorded discharge at 15 min intervals and N the number of observations. As this is a very detailed dataset, this is believed to be an accurate figure.

Table 3. Information on the major sewage treatment works (STW) discharges affecting the Enborne. Locations are shown in Figure 1. Mean flow and mean concentrations are presented based on weekly to monthly measurements made between November 2009 and February 2012.

STW Name	Wash Water	Kingsclere	Greenham Common	Ashford Hill *	Wolverton Townsend *
STW ID	PKEE0126	PKEE0069	PKEE0180	PKEE0012	PKEE0132
Discharge Point	Pound St. Brook	Kingsclere Brook	Enborne	Baughurst Brook	Baughurst Brook
Population Equivalent (PE)	7000	2500	1700	100	50
Distance from monitoring point (km)	15	8	7	4	8
Mean Flow (m^3 s^{-1})	0.026	0.014	0.002	-	-
Mean STW contribution to river flow (%) †	5.13	2.55	0.45	-	-
Max. STW contribution to river flow (%) †	16.5	7.39	3.72	-	-
Ammonia (mg N L^{-1})	2.7	1.8	1.1	5.4	5.1
Oxidised Nitrogen (mg N L^{-1})	18.3	19.4	7.0	30.9	22.9
Orthophosphate (mg L^{-1})	4.42	5.16	4.26	9.31	9.11

Notes: - Data are not available for the specified determinand; † Mean and maximum STW discharge percentage contribution to total river flow was calculated using the mean daily discharge rate from the STW and the mean daily flow at the Brimpton gauging station; * No discharge data are available for Ashford Hill or Wolverton Townsend STW, as the discharge rates are below the requirement for recording.

2.3. Statistical Comparison of High Frequency and Weekly Samples

Comparisons were made using a number of standard techniques, using code written in MATLAB. These included the mean, standard deviation, Pearson correlation coefficient, r [Equation (3)], coefficient of determination, r^2, the Nash-Sutcliffe efficiency criterion, NS [Equation (4)], and the normalised unbiased Root Mean Squared Difference, RMSD*' [Equation (6)]. In addition, the target diagram approach introduced by Jolliff *et al.* [58] was used to provide a visual comparison of bias and pattern agreement between the two datasets. The equations used are detailed below, where m represents the high-frequency data; o the laboratory data; $\bar{m}$ and $\bar{o}$ are the mean of the two datasets; σ_m and σ_o are the population standard deviations of the two datasets; and σ_* is the normalised standard deviation:

$$r = \frac{\frac{1}{n}\sum_{i=1}^{n}(m_i - \bar{m})(o_i - \bar{o})}{\sigma_m \sigma_o} \tag{3}$$

$$NS = 1 - \frac{\sum_{i=1}^{n}(o_i - m_i)^2}{\sum_{i=1}^{n}(o_i - \bar{o})^2} \tag{4}$$

$$\sigma_* = \frac{\sigma_m}{\sigma_o} \tag{5}$$

$$RMSD^{*'} = \sqrt{1 + {\sigma_*}^2 - 2\sigma_* r} \tag{6}$$

$$B^* = \frac{(\bar{m}-\bar{o})}{\sigma_o} \quad (7)$$

$$\sigma_d = sign(\sigma_m - \sigma_o) \quad (8)$$

3. Catchment Overview

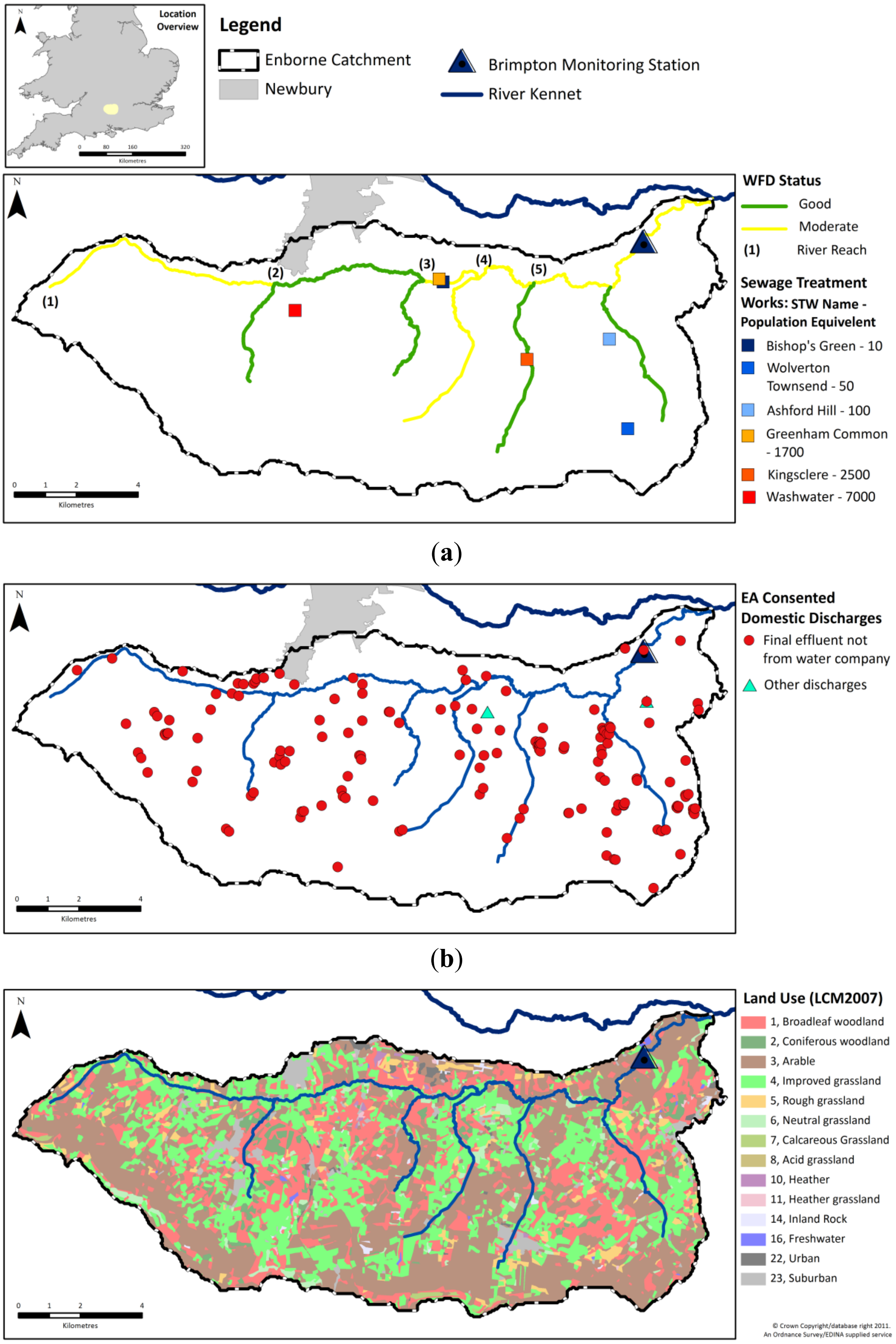
3.1. Land Use

The River Enborne was selected for monitoring as an example of a rural catchment in southeast England with some small population centres. The river drains an area of approximately 148 km^2 and is a tributary of the River Kennet. The river has its source near Ball Hill, southwest of Newbury, Berkshire, UK and joins the River Kennet near the town of Aldermaston (Figure 1). The monitoring station for both flow and chemistry was at Brimpton, about 2 km from this confluence (Figure 1). The relief of the Enborne catchment is characterised by gently sloping valleys with a maximum altitude of 296 m above sea level. The catchment's geology is dominated by Cretaceous Chalk in the headwaters and Tertiary clays in the lower reaches. The long-term annual precipitation over the catchment is 790 mm, though only approximately 35% becomes river flow due to high evapotranspiration and groundwater exports [59]. The baseflow index (the proportion of river flow which is considered baseflow) is 0.53, lower than normal in this area as a result of the impervious clays within the catchment.

Agriculture is the dominant land use within the catchment, with 39% of the catchment designated as "Arable and Horticulture" land under the LCM2007 assessment [48]. The agricultural census data, from 2010, shows that arable crops (defined as arable crops, uncropped and temporary grassland) were the dominant crops accounting for 39% of the agricultural land use, with wheat accounting for 11% [47].

Significant areas of woodland are also present within the catchment, with 21% of the catchment designated as "Broadleaf Woodland" [48]. This woodland is particularly prevalent along the riparian corridor, with 28% of a 1 m buffer zone on either side of the river classified as woodland (Figure 2). The catchment has been identified as having high nature conservation value, with 32 wet woodland Sites of Importance for Nature Conservation (SINCs) identified, including extensive ancient alder woods and associated wet ash maple, and a further 19 SINCs identified for their wet meadows/heath and marshy grassland habitats [60]. There are a number of Sites of Special Scientific Interest (SSSI) in catchment, notably Ashford Hill Woods and Meadows SSSI, which is located to the south of the Brimpton monitoring location and through which the Enborne tributary Baughurst Brook flows (Figure 1c). This site is recognised because of its habitat quality, diversity of communities and number of rare and threatened species, and is without comparison in central southern England [61]. Previous work has identified that aquatic vegetation is sparse in the main river channel [62,63].

Figure 1. The Enborne catchment: (**a**) The Water Framework Directive (WFD) river designations and the sewage treatment work (STW) locations; (**b**) other registered consented domestic discharge locations; (**c**) Land use (from Land Cover Map 2007 [48]).

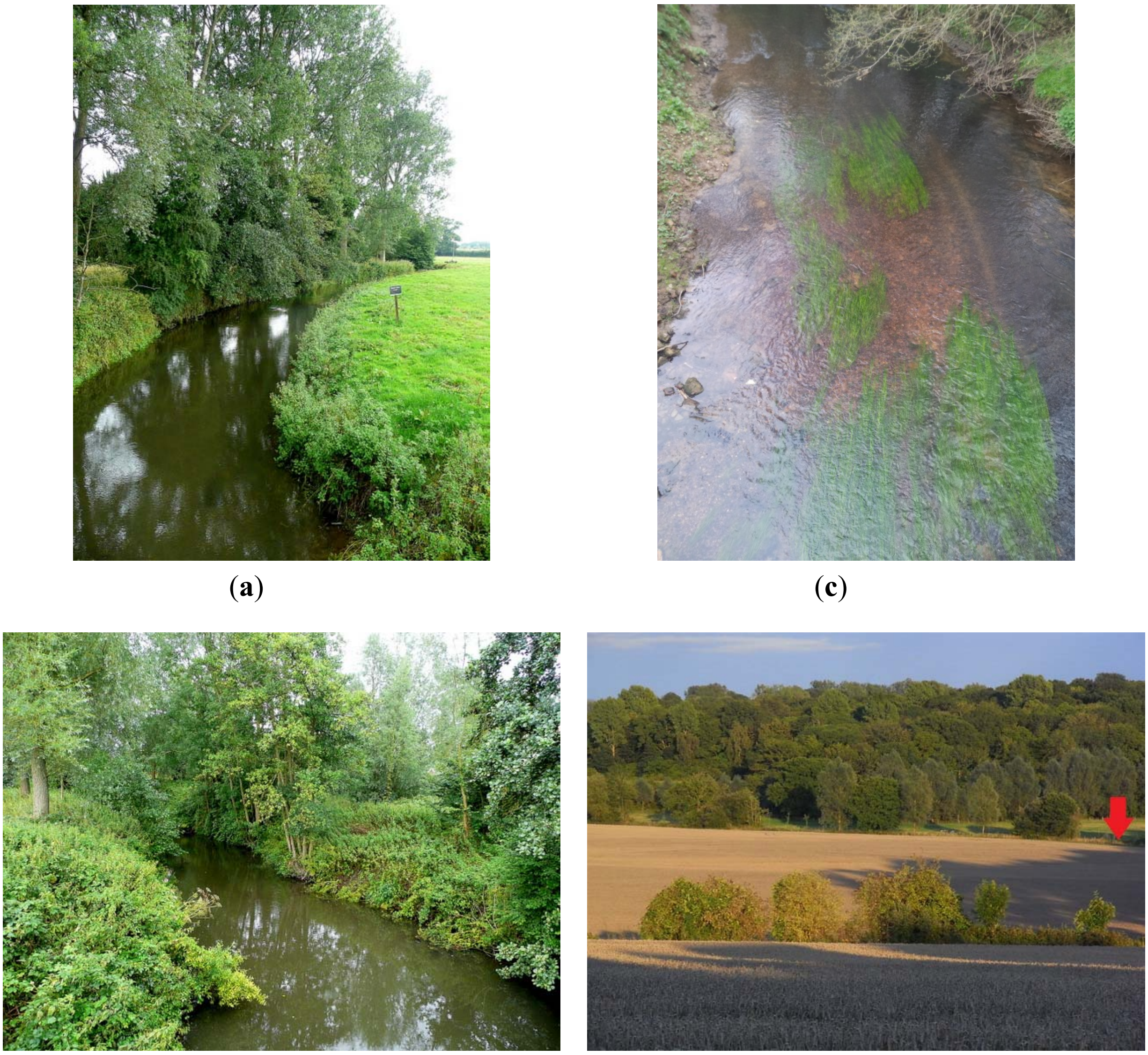


(**a**)

(**b**)

(**c**)

Figure 2. Photographs of the Enborne catchment: (**a**) The River Enborne—view upstream from Shalford Bridge (SU569649) on 31 July 2009; (**b**) view downstream from Shalford Bridge on 31 July 2009 both © copyright Jonathan Billinger and licensed for reuse under a Creative Commons Licence (CCL); (**c**) Macrophyte growth on the River Enborne (SU557633), just upstream of its confluence with Baughurst Brook on 31 March 2012; and (**d**) Fields of wheat near the river (arrow), 27 August 2013 (SU560647) © Andrew Smith CCL).



(**a**) (**c**)

(**b**) (**d**)

The resident population of the catchment was estimated to be 18,260 people in 7240 households. This gives a population density of 123 persons km^{-2}, significantly lower than the average of southeast England (excluding London) of 450 persons km^{-2}. Most are located in small settlements and isolated groups of houses, with a small part of the large town of Newbury in the northwest of the catchment (Figure 1). There is no large-scale industry, the largest facility being the Greenham Common Airbase on the north boundary of the catchment. This probably introduces some sewage inputs from non-residents via the Greenham Common STW (see below).

3.2. Water Resources

The catchment provides water for public and industrial supply, with 27 licensed abstraction points in the Enborne Water Resource Management Unit (WRMU): 17 groundwater and 10 surface water [64]. Despite the largely rural nature of the catchment there are six STWs within the catchment, with two discharging directly to the main river (Figure 1a and Table 3): Greenham Common, PE 1700, and Bishop's Green, PE 10.

Both Greenham Common and Bishop's Green STWs 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 Pound Street Brook (PE 7000), at Kingsclere on Kingsclere Brook (PE 2500), and at Ashford Hill (PE 100) and Wolverton Townsend (PE 50) on Baughurst Brook (Figure 1a). All enter the River Enborne upstream of the Brimpton monitoring site. As a rural catchment, the river system is also affected by septic tank discharges, which can discharge directly to the Enborne or one of its tributaries (Figure 1b). The rural nature of the Enborne catchment means there is a high density of septic tank systems (STS) throughout the catchment with 163 registered consented domestic discharges, 78 of which are assigned as discharging directly to the catchment's river system [65]. The distribution of these is shown in Figure 1b. However, we estimate there are approximately 2600 unregistered STSs (see Section 2.2). There are also 81 non-domestic consented discharges in the catchment (mostly small sources such as hotels, dog boarding kennels, *etc*.).

3.3. Legislative Designations

The WFD defines five classes of ecological status for surface waters: high, good, moderate, poor or bad, with the status determined by assessing four aspects of surface water quality: biological; physico-chemical; hydromorphological; and chemical [66]. The overall status assigned to a water body is determined by the lowest status met under all criteria, *i.e.*, if the water body achieves good biological quality but poor hydromorphological quality, the ecological status of the water body would be poor [66]. Under the UK's implementation of the WFD, the Enborne is classified as a lowland, high-alkalinity system and all reaches/tributaries of the Enborne have a typology of "low, small and calcareous", implying that the mean altitude of each reach is <200 m, the reach area is 10–100 km^2 and the dominant geology is calcareous (based on British Geological Survey 1:25,000 geology data). The current status of the system varies between "moderate" and "good" depending on the river reach (Figure 1a and Table 4). In terms of the physico-chemical parameters considered under the WFD, in order for the Enborne to achieve a good or high status the following criteria must be met:

- Dissolved oxygen: The 10th percentile of the dissolved oxygen time series must be greater than 60% saturation for "good" and 70% for "high";
- Phosphorus: Mean annual soluble reactive phosphorus (SRP) concentration must be less than 0.12 mg P L^{-1} for "good" and less than 0.05 mg P L^{-1} for "high";
- pH: The 5th percentile of the pH time series must be greater than 6.0 and the 95th percentile less than 9.0 for "good/high".

According to EA monitoring, these criteria are being met on all reaches of the River Enborne except the lowest one.

Table 4. Information on the current WFD status for the River Enborne and its tributaries.

River Reach	**Source to A34 (1)**	**A34 to Burghclere (2)**	**Burghclere to Ecchinswell (3)**	**Ecchinswell to Kingsclere (4)**	**Kingsclere to Kennet (5)**
Ecological Quality Status					
Current	Moderate	Good	Moderate	Moderate	Moderate
Predicted 2015	Moderate	Good	Moderate	Moderate	Moderate
Overall Biological Quality	**Moderate**	-	**Moderate**	**Moderate**	**Moderate**
Fish	Moderate	-	Moderate	Moderate	Moderate
Macro-invertebrates	-	-	Good	High	Good
Macrophytes	-	-	-	-	-
Overall Physico-chemical Quality	-	**Good**	**Good**	**Good**	**Moderate**
Ammonia	-	High	High	High	High
Dissolved Oxygen	-	Good	Good	Good	High
pH	-	High	High	High	High
Phosphate	-	Good	Good	Good	Moderate
Overall Hydromorphological Quality	**Not High**	**Not High**	**Not High**	**Not High**	**Not High**
Hydrology	High	Not High	Not High	Not High	Not High
Morphology	Good	Good	Good	Good	Good
Overall Specific Pollutant Quality	-	**High**	**High**	**High**	**High**
Ammonia	-	High	High	High	High
Copper	-	-	-	-	High
Zinc	-	-	-	-	High

4. Results

4.1. Comparison of in Situ *and Laboratory Instrumentation*

The *in situ* and laboratory data were highly correlated for all 5 measurements considered (Table 5). The “goodness of fit” statistics calculated (RMSD and Nash-Sutcliffe) also indicate that for TRP, NO_3, temperature and conductivity there is a high degree of consistency between both sets of measurements (Table 5). However, the *in situ* and laboratory pH measurements did show marked differences. These results are summarised in the normalised target diagram (Figure 3a). These diagrams were introduced by Jolliff *et al.* [58] as a visual comparison of modelled and observed data, but can also be used (as here) to compare any two sets of data.

For TRP, NO_3, temperature and conductivity, agreement was excellent whereas for pH the high-frequency data showed a positive bias and the dataset had a larger standard deviation (Figure 3). These features are evident when the two pH time series are compared, with pH of the weekly grab sample data in general slightly lower than the pH recorded by the *in situ* instrumentation (Table 5 and Figure 4). The occurrence of lower pH measurements in the laboratory analysis may result from nitrification of ammonium (NH_4) and dissolved organic nitrogen (DON) or through ammonia (NH_3) degassing in the water sample prior to analysis. pH electrodes can also suffer problems such as accurate calibration and drift [39]. Despite these observations, the average difference in pH between the two measurements was only 0.25, and both datasets displayed the same pattern and range in pH.

Given these small differences between the *in situ* and laboratory readings, for the purposes of this work the high-frequency pH datasets have been utilised.

Table 5. Goodness of fit statistics between the traditional laboratory hydrochemical measurements (Lab) and the measurements made *in situ* by the high-frequency equipment (HF).

Statistic	Dataset	TRP	NO_3	Temperature	Conductivity	pH
Mean	HF	0.18	4.01	10.3	492	7.98
	Lab	0.19	4.02	10.7	496	7.73
Standard Deviation	HF	0.08	0.68	4.61	72.0	0.22
	Lab	0.07	0.66	4.84	85.2	0.19
No. Measurements		12	101	107	89	106
Pearson's Correlation Coefficient (r)—[Equation (3)]		0.84^{***}	0.92^{***}	0.98^{***}	0.90^{***}	0.80^{***}
Coefficient of determination (r^2)		0.70	0.84	0.97	0.80	0.64
Normalised Unbiased Root Mean Squared Difference [RMSD*'—Equation (6)]		0.59	0.42	0.19	0.45	0.72
Nash Sutcliffe [NS—Equation (4)]		0.64	0.82	0.96	0.80	−1.34

Notes: Correlation is statistically significant at: *** $p < 0.001$; ** $p < 0.01$; * $p < 0.05$.

4.2. Mass Balance of Catchment Nutrients

To further characterise the catchment, the major inputs and outputs of N and P were calculated (Table 6—methods given in Section 2.2). For both N and P, agricultural fertiliser inputs, especially to arable land, dominate the input loads, though atmospheric N deposition was also significant. Inputs from human sewage, whether from STWs or STSs, are much smaller. However, this is not necessarily reflected in their influence on the river (see below). Of the estimated annual loads received by the catchment, approximately only 4% of the P and 9% of the N leaves the catchment in the river. This is however only a partial mass balance performed to illustrate the relative importance of these sources and sinks to the system. Although not monitored as part of this work, water, and thus N and P, can also enter and leave the catchment in groundwater, and as the Enborne is a groundwater-dominated catchment this may be a significant source and/or sink. Historic groundwater monitoring in the wider Kennet catchment has previously identified significant N and P pollution, with mean NO_3 concentrations between 1998 and 2000 ranging between 4.6 and 5.9 mg N L^{-1} in the upper Kennet [45]. In addition, water, N and P are exported in agricultural products, and there may be more agricultural inputs in the form of animal feedstuffs. Nevertheless it illustrates that to understand the controls on N and P concentrations in the river, the fate of the N and P from individual sources must be carefully modelled [67].

Figure 3. (**a**) Target diagram showing normalised unbiased RMSD [RMSD$^{*'}$—Equation (6)] multiplied by the sign of the standard deviation difference [σ_d— Equation (8)] against the normalised bias [B*— Equation (7)] between the high-frequency/laboratory results. Results in the inner circle are considered to have excellent agreement, those in the outer circle to have good agreement. Subplots (**b**)–(**f**) show the *in situ* high-frequency measurements (y-axis) plotted against the laboratory measurements (x-axis) for each determinand.

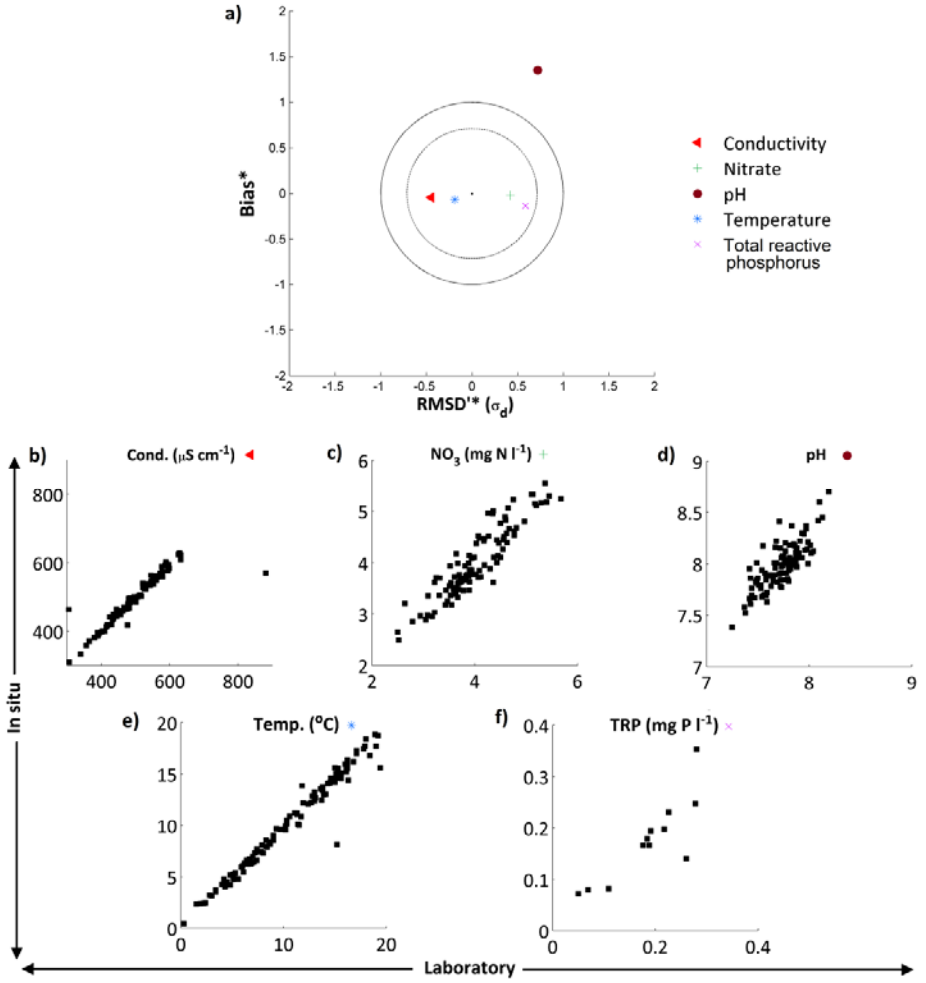


Table 6. Partial mass balance for P and N in the Enborne catchment [*].

System inputs	Estimated annual load (kg P yr^{-1})	% of total load	Estimated annual load (kg N yr^{-1})	% of total load
Atmospheric deposition	3,150	3.7	233,000	19.2
Sewage: STWs	6,570	7.8	28,500	2.4
STSs	3,730	4.4	17,300	1.4
Fertiliser: Arable	56,000	66.6	691,000	57.1
Grassland	14,600	17.4	241,000	19.9
Total	**84,050**	**100.0**	**1,210,800**	**100.0**
System Outputs				
Riverine load	3,100	3.7	107,200	8.9

Note: [*] It is recognised that the mass balance is partial as other inputs and outputs of N and P such as in the groundwater have not been accounted for (see above text).

4.3. Overall Water Chemistry

Water quality statistics for the River Enborne are shown in Table 7. Where available, data are shown for three independent datasets: the high-frequency data (HF) were measured hourly as described in Section 2.1, and there were two datasets of weekly measurements, measured on different days: Thames Initiative (TI) data and LIMPIDS ground-truthing data (GT) [38]. Time courses for selected determinands from the weekly and hourly datasets are shown in Figure 4. Only some of the major features of these data will be discussed in this paper—subsequent papers will examine the data in more detail. Baseflow water in the river is dominated by calcareous groundwater from the chalk aquifer, accounting for the high alkalinity, high calcium (Ca) and conductivity, and pH in the upper 7–8 range. During stormflow Ca concentrations are approximately halved on average, but concentrations remains high, with alkalinity and conductivity responding in the same way (Table 7, Figure 4).

Table 8 shows rank correlation coefficients between the concentrations of various determinands. Positive correlations with Ca may imply a groundwater source—this applies to silicon (Si), for instance, while dissolved organic carbon (DOC) has a strong negative correlation, showing an origin in surface runoff, as expected. N and P species also have a highly significant correlation with Ca. However, periods with a high groundwater contribution are low flow periods when the dilution capacity of the system is also reduced. Therefore, higher N and P concentrations observed at these times may be the result of poor dilution of agricultural and sewage nutrient sources under low flows, rather than an increased contribution of nutrient enriched groundwater. Indeed, TRP correlates (negatively) with flow even better than it does with Ca, suggesting that poorer dilution of a constant point source is the predominant explanation, whereas NO_3 correlates better with Ca than with flow, suggesting that there is a groundwater contribution to river NO_3, which is consistent with the high groundwater NO_3 concentrations in the adjacent Pang and Lambourn catchments and upper reaches of the Kennet [45,68]. Other features of the overall water chemistry show clear anthropogenic influences in the high N and P concentrations and other markers such as boron (largely derived from detergents). Dissolved oxygen is clearly also affected but still at an acceptable level.

4.4. Nitrogen and Phosphorus Speciation

Based on the weekly grab samples, dissolved P was also found to dominate the P composition, with total dissolved P (TDP) accounting for, on average, 78% of the total P (TP) and particulate P (PP) only 22% (Figure 5). In addition, the majority of the TDP, on average 81%, was in soluble reactive form (SRP; Figure 5). The monitoring equipment used in the Enborne high-frequency monitoring scheme measured TRP instead of SRP. SRP is traditionally regarded as a better measure of bioavailable P and is the basis for UK legislative standards. The difference between these two P fractions is that for SRP the sample is filtered prior to analysis, consequently TRP concentrations are usually slightly higher as readily hydrolysable-particulate P fractions are included in the measurement. Weekly measurements of TRP and SRP were performed on different days (Table 7), but a good correspondence between them was observed, and the weekly SRP measurements were significantly positively correlated to the high-frequency TRP recorded on the same hour as sample collection ($\rho = 0.89$, $p < 0.001$;

$SRP_i = 0.81*TRP_i$; Figure 6). Therefore, the recorded TRP concentrations on the Enborne are assumed to provide a reasonable estimate of the streamwater SRP concentrations.

Table 7. Water quality statistics for the River Enborne.

Determinand	**Units**	**Dataset**[*]	**Mean**	**Stormflow Mean**	**Baseflow Mean**	**Min**	**Max**
Flow	$m^3 s^{-1}$	15 min	1.07	4.76	0.14	0.09	25.1
Temperature	°C	TI	10.4	6.58	15.0	−0.2	19.4
		HF	10.3	6.71	14.4	0.19	20.3
pH	n/a	TI	7.72	7.48	7.76	7.25	8.19
		HF	7.97	7.71	7.95	7.24	8.94
Conductivity	$\mu S\ cm^{-1}$	GT	496	360	568	305	881
		HF	477	344	559	215	769
Alkalinity	$\mu Eq\ L^{-1}$	TI	2800	1850	3430	1190	4350
Turbidity	NTU	HF	8.74	31.3	6.09	2	387
DO	% Sat	HF	90.3	95.8	73.5	53	170
TDP [+]	$mg\ P\ L^{-1}$	TI	0.16	0.09	0.23	0.07	0.34
SRP	$mg\ P\ L^{-1}$	TI	0.13	0.07	0.2	0.02	0.31
TRP	$mg\ P\ L^{-1}$	HF	0.17	0.08	0.23	0.00	0.6
		GT	0.15	0.09	0.23	0.05	0.35
PP	$mg\ P\ L^{-1}$	TI	0.04	0.08	-	0.02	0.12
TP	$mg\ P\ L^{-1}$	TI	0.20	0.17	0.27	0.09	0.45
NO_3	$mg\ N\ L^{-1}$	HF	3.96	3.28	4.35	1.7	6.24
		TI	3.97	3.38	4.44	2.41	5.68
NH_4	$mg\ N\ L^{-1}$	TI	0.06	0.07	0.04	0.00	0.28
DON [±]	$mg\ N\ L^{-1}$	TI	0.43	0.45	0.30	0.00	1.19
TDN	$mg\ N\ L^{-1}$	TI	4.35	3.88	4.61	2.4	6.31
DOC [†]	$mg\ L^{-1}$	TI	5.81	7.84	3.83	1.19	11.8
Si	$mg\ L^{-1}$	TI	7.00	5.40	8.61	2.96	9.9
Na	$mg\ L^{-1}$	TI	19.1	15.1	24.8	11.1	31.4
K	$mg\ L^{-1}$	TI	3.73	3.67	4.47	2.49	6.15
Ca	$mg\ L^{-1}$	TI	68.5	48.1	81.5	36.5	99.5
Mg	$mg\ L^{-1}$	TI	4.41	4.45	4.15	2.75	6.02
Cl	$mg\ L^{-1}$	TI	36.8	29.4	45.0	22.4	60.1
SO_4	$mg\ S\ L^{-1}$	TI	9.16	8.15	8.43	6.36	12.0
B	$\mu g\ L^{-1}$	TI	26.8	24.5	29.2	20.8	37.5
Al	$\mu g\ L^{-1}$	TI	22.3	108	6.90	1.08	184
Fe	$\mu g\ L^{-1}$	TI	116	250	56.6	19.2	434

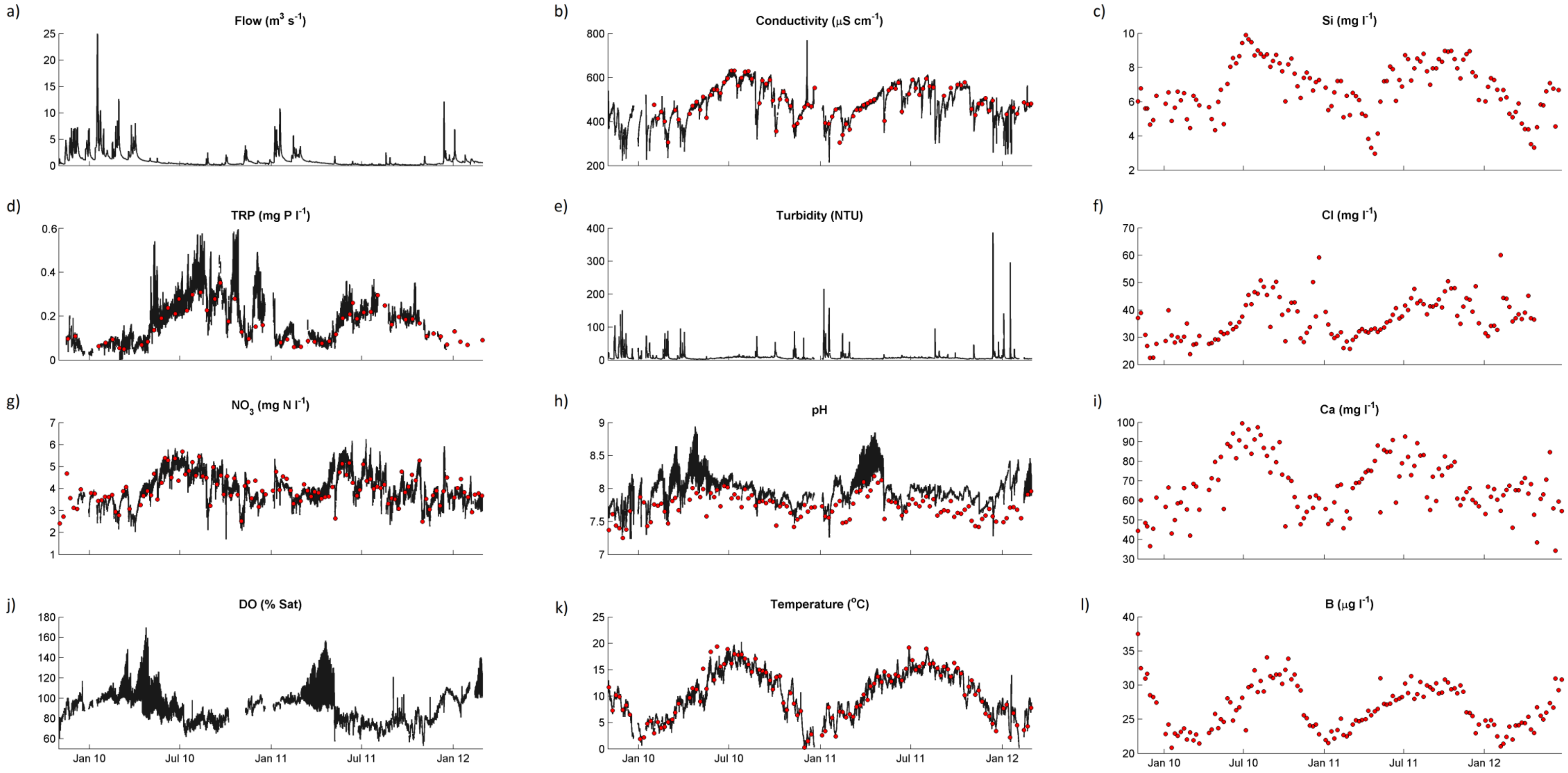
Notes: - Data are not available for the specified determinand; [*] HF = LIMPIDS high-frequency data; TI = CEH Thames Initiative data; GT = LIMPIDS ground-truthing data; [+] Phosphorus abbreviations: TDP, total dissolved P; SRP, soluble reactive P; TRP, total reactive P; PP, particulate P; TP, total phosphorus; these are defined below; [±] Nitrogen abbreviations: DON, Dissolved organic N; TDN, Total dissolved N; [†] DOC data were limited for the period of record with only 77 measurements.

Table 8. Spearman's rank correlation coefficients (ρ) between the water quality parameters (*** $p < 0.001$; ** $p < 0.01$; * $p < 0.05$).

	Flow	**Temp.**	**pH**	**Cond.**	**Turb.**	**DO**	**TRP**	**PP**	**TP**	**NO_3**	**DON**	**TDN**	**DOC**	**Si**	**Ca**	**Cl**
Flow																
Temp.	-0.65^{***}															
pH	-0.32^{***}	0.33^{***}														
Cond.	-0.82^{***}	0.71^{***}	0.63^{***}													
Turb.	0.06	0.21^{*}	-0.41^{***}	−0.04												
DO	0.67^{***}	-0.62^{***}	0.19	-0.51^{***}	-0.39^{***}											
TRP	-0.77^{***}	0.59^{***}	0.21	0.79^{***}	0.19	-0.69^{***}										
PP	−0.12	0.37^{***}	−0.11	0.21^{*}	0.63^{***}	-0.35^{***}	0.32^{**}									
TP	-0.65^{***}	0.72^{***}	0.1	0.67^{***}	0.52^{***}	-0.76^{***}	0.81^{***}	0.60^{***}								
NO_3	-0.46^{***}	0.59^{***}	0.45^{***}	0.73^{***}	0.2^{*}	-0.41^{***}	0.55^{***}	0.22^{*}	0.52^{***}							
DON	−0.04	0.18	0.00	0.03	0.22	0.00	0.13	0.25^{*}	0.08	0.15						
TDN	-0.26^{**}	0.31^{**}	0.41^{***}	0.55^{***}	0.13	−0.16	0.45^{***}	0.14	0.29^{**}	0.82^{***}	0.36^{***}					
DOC	0.36^{**}	-0.27^{*}	-0.71^{***}	-0.54^{***}	0.11	0.04	−0.23	0.07	−0.19	-0.56^{***}	0.14	-0.44^{***}				
Si	-0.74^{***}	0.52^{***}	0.08	0.69^{***}	0.10	-0.66^{***}	0.8^{***}	0.13	0.67^{***}	0.45^{***}	−0.11	0.36^{***}	−0.25			
Ca	-0.68^{***}	0.68^{***}	0.74^{***}	0.94^{***}	−0.14	-0.34^{***}	0.63^{***}	0.11	0.50^{***}	0.78^{***}	0.04	0.58^{***}	-0.72^{***}	0.56^{***}		
Cl	-0.74^{***}	0.39^{***}	0.13	0.74^{***}	0.12	-0.61^{***}	0.82^{***}	0.18	0.60^{***}	0.30^{**}	−0.01	0.15	−0.23	0.62^{***}	0.41^{***}	
B	-0.63^{***}	0.67^{***}	−0.09	0.42^{***}	0.24^{*}	-0.74^{***}	0.58^{***}	0.32^{***}	0.69^{***}	0.35^{***}	0.10	0.08	0.08	0.45^{***}	0.31^{***}	0.34^{***}

Notes: Temp. = Temperature; Cond. = Conductivity; Turb. = Turbidity; DO = Dissolved Oxygen; TRP = Total Reactive Phosphorus; PP = Particulate P; TP = Total P; DON = Dissolved Organic Nitrogen; TDN = Total Dissolved N; DOC = Dissolved organic carbon.

Figure 4. Concentrations of selected chemical determinands in the River Enborne at Brimpton during the study period: black lines, hourly data; red points, weekly data. (**a**) Flow; (**b**) Conductivity; (**c**) Silicon; (**d**) Total reactive phosphorus; (**e**) Turbidity; (**f**) Chloride; (**g**) Nitrate; (**h**) pH; (**i**) Calcium; (**j**) Dissolved oxygen; (**k**) Temperature; and (**l**) Boron.



NO_3 was the dominant form of N in the Enborne, accounting for on average 89% of the total dissolved N (TDN); with nitrite (NO_2) accounting for less than 1%, ammonium (NH_4) for approximately 1% and dissolved organic nitrogen (DON) approximately 9% (Figure 5). The high proportion of NO_3 reflects the view of the EU Nitrogen Assessment [14] that systems like the Enborne are at the high end of the oligotrophic—hypertrophic gradient and, although DON concentrations are also high, they form a smaller proportion of the total dissolved N. No seasonality was observed within the nutrient species composition, with NO_3 and SRP dominating the N and P composition throughout both years.

Figure 5. Mean annual percentages of different P and N species in the Enborne. SRP, soluble reactive P; DHP, dissolved hydrolysable P; PP, particulate P; TDP, total dissolved P; DON, dissolved organic N.

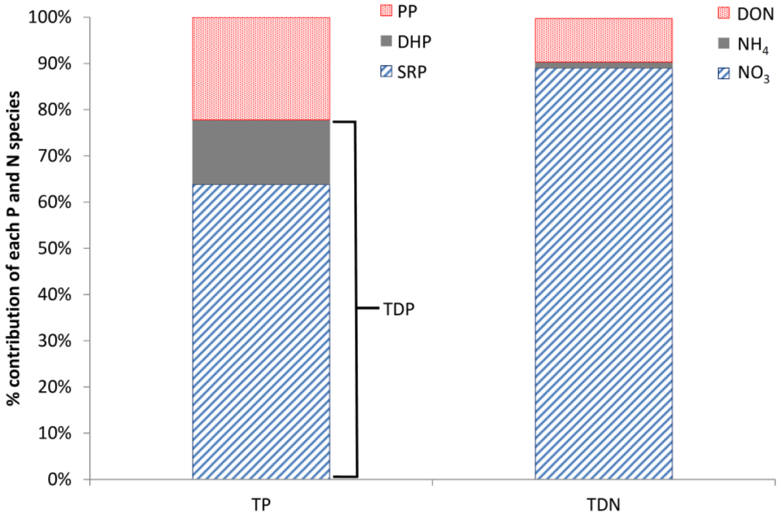
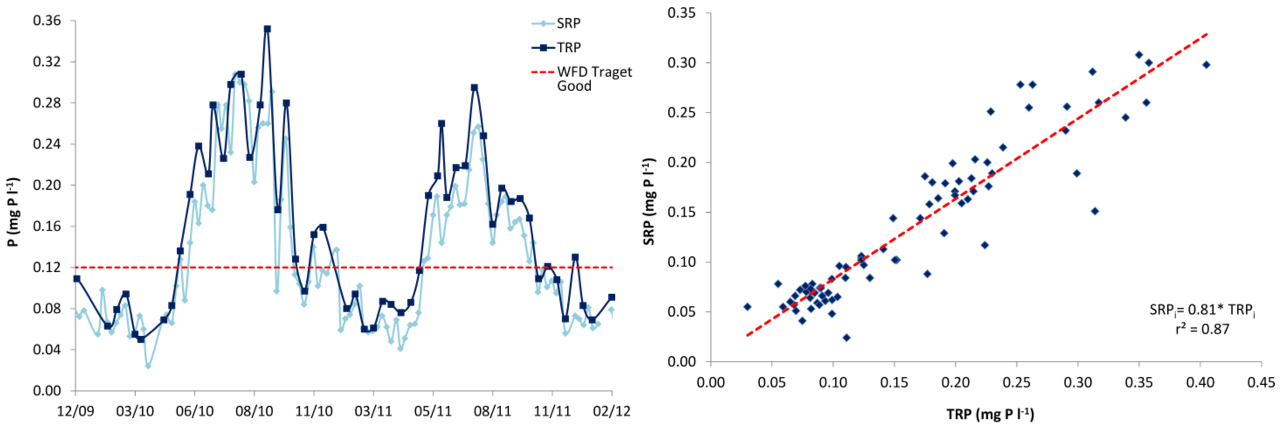


Figure 6. (**a**) Soluble reactive P (SRP) and total reactive P (TRP) concentrations in weekly grab samples (on different days) in the Enborne at Brimpton. The mean annual target concentration under the Water Framework Directive is also shown; (**b**) The relationship between SRP in the grab samples and TRP in the high-frequency samples taken at the same time.



(**a**) (**b**)

4.5. Chemical Dynamics

The 2-year time series is too short to provide an indication of trends over time. However, the variability in concentrations is dominated by seasonal variation (Figure 4), and some mechanistic deductions can be made from these data.

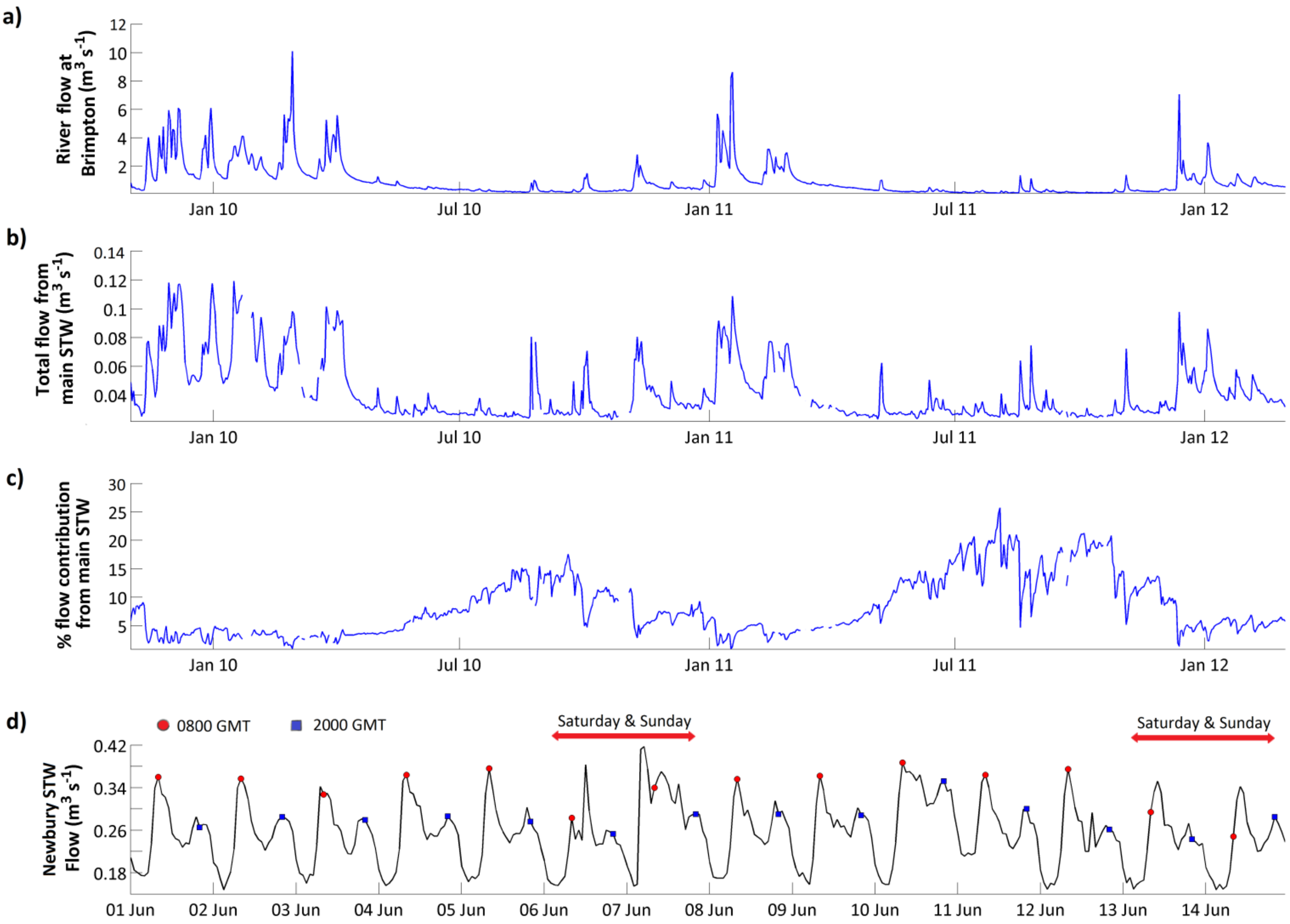
Figure 4a shows the Enborne responding rapidly to rainfall events, especially in the winter and spring when the catchment soils are wet. In the summer there are long periods of low flows when the river is sustained by groundwater and inputs from human sources. Figure 7a–c shows river flow at the Brimpton monitoring point and discharges from the major STWs over the same period. During the winter and in storm events, the STWs contribute around 4% of the overall river flow, even though water flux through the STWs increases during storm events (Figure 7b). During low flows, however, the STWs contribute a much higher proportion of river flow, reaching 27.6% in summer 2011 (Figure 7c; Table 3), so that the average contribution of STWs to flow during the entire monitoring period is 8.1% (Table 3). Wade *et al.* [38] also identified a two-peak diurnal cycle in the Brimpton flow, TRP and NO_3 time series during periods of low flow. This was linked to periods of greater domestic water consumption in the morning and evening [24,69,70]. High-frequency discharge measurements are not available from the Enborne catchment STWs, but Figure 7d, showing discharge from the adjacent Newbury STW during 2009, shows this very clearly, with a sharp morning peak and a broader peak in the evening during the working week, and a more irregular pattern at weekend.

A seasonal pattern of concentration can be seen very clearly in most of the determinands in Figure 4, with generally higher concentrations in summer. Much of this can be explained by the lower dilution capacity of the river in summer. There are also strong correlations with flow, mostly negative (Table 8). However, the high-frequency nutrient measurements reveal a complex system with subtle variations in dilution and concentration. The complex TRP-flow dynamics are discussed in detail in Wade *et al.* [38] and result from the combination of both point and diffuse sources of P as well as resuspension of bed material. For NO_3 the negative relationships with flow arose because the time series was dominated by significant dilutions of NO_3 concentration during high flow events, although occasional increases in NO_3 concentration with flow can be observed, for example in January 2011 (Figure 4).

Figure 4 also shows that responses and relationships can differ with season. Diurnal variation in pH (Figure 4h) and dissolved oxygen (Figure 4j), visible as a thick line in the Figure, are clearly related and have an especially large amplitude in spring. This is due to the photosynthesis—respiration diurnal cycle which affects both variables, but the relationship breaks down at other times of year, and thus the overall correlation in Table 8 is not significant. These more complex relationships will be addressed in subsequent papers using the high-frequency data. In this paper, we will only consider the high-frequency data in relation to turbidity and conductivity (see Section 4.6 below).

Unusually high chloride (Cl) peaks in winter (Figure 4f) correlate with unusually high sodium (Na) peaks and are almost certainly due to washoff of de-icing salt from roads—a major trunk road, the A34, crosses the upper part of the river near the Washwater STW (Figure 1a). Otherwise Cl is influenced by seasalt deposition, both current and preserved in groundwater, and sewage effluent. The predominantly "hard" water in the area implies use of NaCl to regenerate water softeners, and this NaCl appears in the STW and septic tank effluents.

Figure 7. (**a**) Measured flow at Brimpton; (**b**) measured discharges from the three major sewage treatment works (Table 3); (**c**) Percentage contribution of STW discharges to observed river flow at Brimpton; (**d**) discharge from Newbury STW in June 2009, showing diurnal patterns.

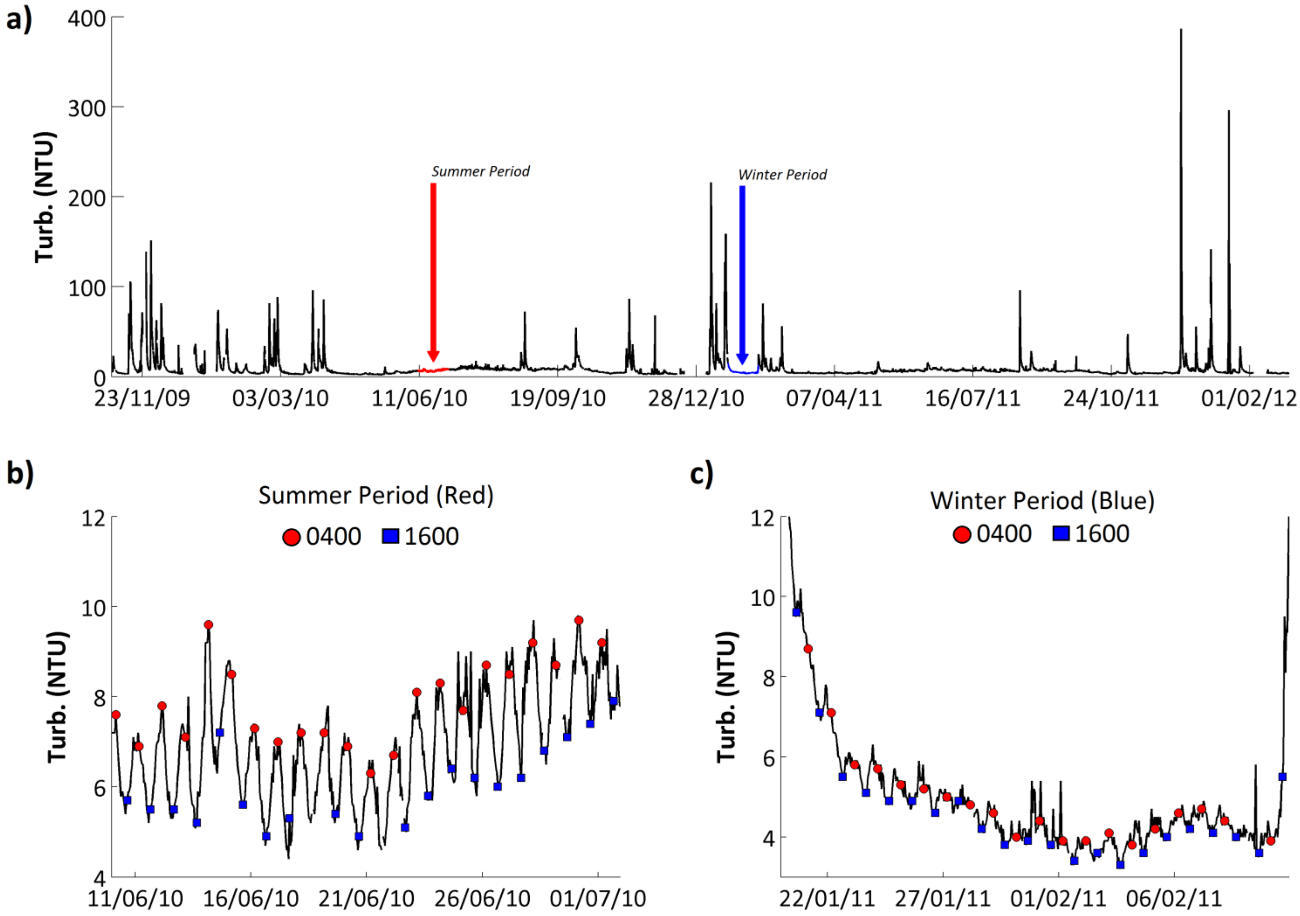


4.6. High Frequency Analysis of Turbidity and Conductivity Data

Turbidity on the Enborne ranged from 2 to 387 Nephelometric Turbidity Units (NTU), with a mean value of 8.7 NTU (Figure 8; Table 7). Overall, the turbidity time series was dominated by large peaks associated with high flow events (Figure 8a), with turbidity values increasing by over 3 orders of magnitude in one day, before dropping back to the baseline value. Because high flows tend to occur in the winter months, the highest turbidity values tend to occur in winter too. A strong but small amplitude diurnal cycle was identified in the turbidity time series during low flow periods (Figure 8b,c). The amplitude of the diurnal variations were larger in the spring and summer months, >4 NTU (Figure 8b), and decreased in the autumn and winter, <1 NTU, with the signal completely disappearing during high flow events (Figure 8c).

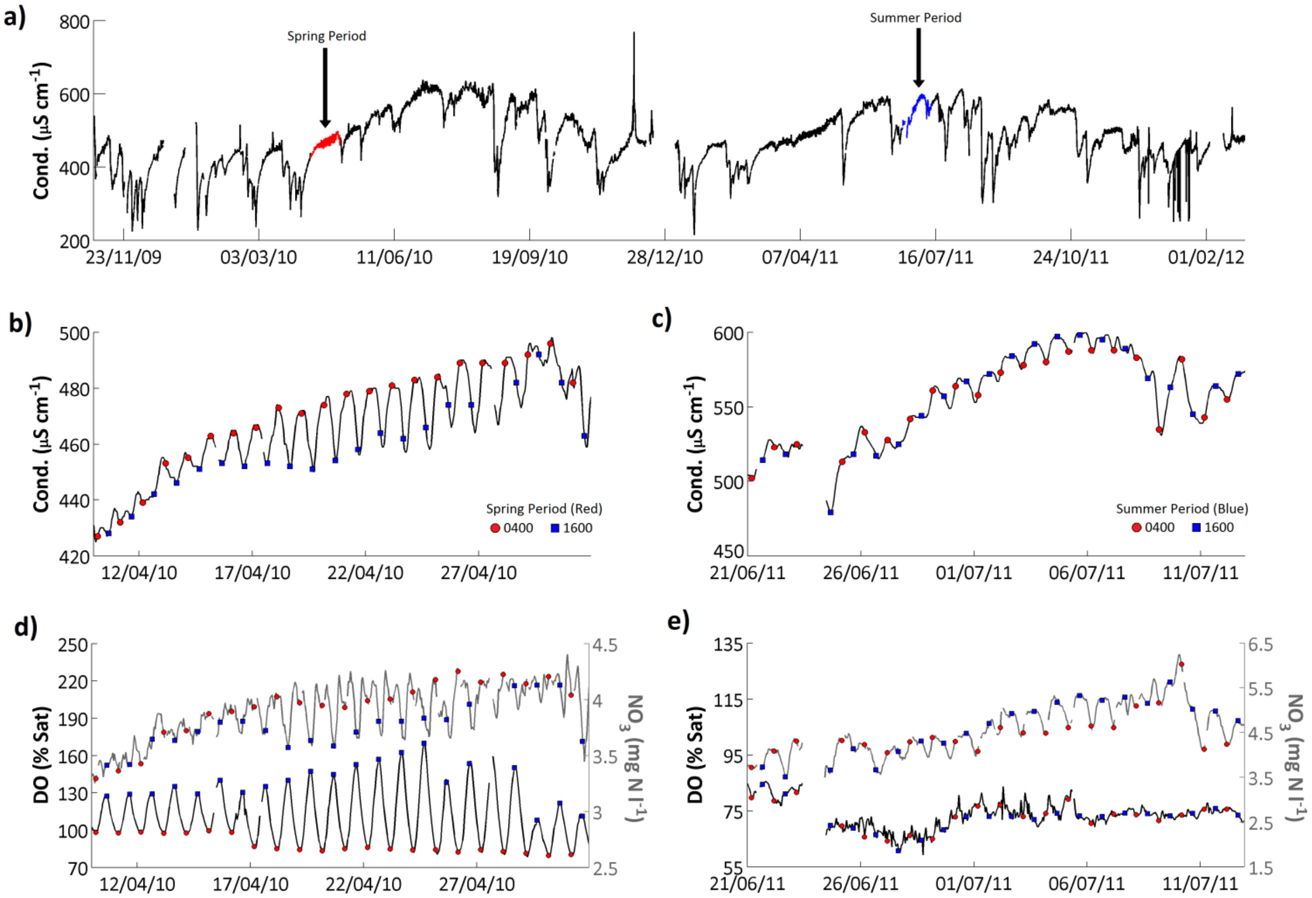
The phase of the diurnal turbidity cycle was consistent, with peak turbidity observed in the night at approximately 0400 GMT and minimum turbidity levels in the afternoon at approximately 1600 GMT (Figure 8b,c). This type of turbidity cycle has been identified in other rivers and attributed to nocturnal feeding and movement of fish, invertebrates and other stream biota [71,72]. In one of these papers high nighttime turbidity values coincided with increased total suspended P loading [71]. This was also found on the Enborne, with a strong positive correlation between PP and turbidity (Table 8). In addition, at certain periods throughout the study, particularly in the mid to late summer, elevated TRP concentrations were also observed in the night alongside maximum turbidity concentrations.

Figure 8. (**a**) Hourly turbidity record from the River Enborne at Brimpton. Two low-flow periods, one in summer (**b**) and one in winter (**c**), are highlighted and shown in expanded form, respectively. In these figures, the 0400 and 1600 GMT data points are highlighted for convenience.



Conductivity ranged from 215 to 769 µS cm^{-1} and had a mean value of 477 µS cm^{-1} on the Enborne (Figure 9; Table 7). Conductivity is affected by any charged species, and the causes of the observed patterns varied over time. Based on an analysis of the determinands measured as part of the weekly grab sampling programme, conductivity was high on the Enborne as a result of high Ca concentrations (accounting for approximately 37% of the conductivity); and high Cl concentrations (15%). Overall the conductivity signal showed a very similar seasonality to the NO_3 signal (Figure 4), with peak values in the late spring/early summer. Additionally conductivity was closely related to flow with large flow peaks corresponding directly to significant reductions in conductivity ($\rho = -0.40$, $p < 0.001$, for high-frequency data; Table 8). Even small flow events were found to significantly reduce the streamwater conductivity when the antecedent catchment conditions had been very dry.

Figure 9. (**a**) Hourly conductivity record from the River Enborne at Brimpton. Representative (**b**) spring and (**c**) summer periods are highlighted and shown in expanded form, respectively; (**d**) shows dissolved oxygen and (**e**) nitrate concentrations for the same periods; In (**b**–**d**), the 0400 and 1600 GMT data points are highlighted for convenience.



Although, as with turbidity, larger amplitude fluctuations in conductivity were controlled by the changes in flow, relatively small amplitude, on average 25 µS cm^{-1}, diurnal fluctuations can also be observed within the time series (Figure 9b,c). Although these diurnal variations in conductivity are small compared to the full conductivity range on the Enborne, in comparison to the range of conductivity values observed in UK rivers, as low as 30 µS cm^{-1} in some upland systems, these diurnal variations are significant. The diurnal cycle phase was highly variable. In the early spring a one-peak cycle was dominant in which conductivity peaked in the early morning and reached a minimum in the evening (Figure 9b). These springtime daily variations in streamwater conductivity were likely caused by the diurnal changes in respiration/photosynthesis. This was supported by the occurrence of minimum dissolved oxygen at the same time as maximum conductivity (0400 GMT; Figure 9d), which also coincides with a pH minimum, consistent with the night-time increase in carbonic acid species through the release of CO_2 during respiration. The night-time increase in conductivity was thus largely due to increased bicarbonate (HCO_3^-) concentrations derived from respired CO_2. In the late summer, peak conductivity timing changed to during the late afternoon (Figure 9c). Although bicarbonate would still have been relatively low at this time, the photosynthetically-driven cycle of bicarbonate concentration was reduced in the summer, probably as a result of riparian shading along the course of the river, as evidenced by the irregular dissolved oxygen cycle at this time (Figure 9e). Instead during the summer the bicarbonate signal is swamped by the larger-amplitude cycle of nitrate concentrations, which peak in the daytime due to increased nitrification (Figure 9e). Additionally, the two peak diurnal cycles observed in the N and P signals at low flow periods, resulting from the influence of STW discharges, could also be contributing to the diurnal dynamics observed in the conductivity signal. This is supported, at certain periods, by the occurrence of two peak structure in the conductivity diurnal dynamics, however the amplitude of the two peak structure is extremely small (<5 μS cm^{-1}). These considerations illustrate the difficulties of interpreting detailed conductivity data without supporting concentration measurements.

5. Discussion

5.1. Influences on Water Quality—Insights from Flow and Nutrient Dynamics

Comparison of the weekly, laboratory-based methods and the automated high-frequency methods (Section 4.1) shows that both give comparable results, with an indication that, with this water, pH can fall slightly between sampling and laboratory measurement a few hours later. This, however, is not sufficient to affect the interpretation of results. The overall water chemistry is of a river fed by calcareous groundwater, which is diluted during storms and when catchment water levels are high, such as during winter. However, there is clear evidence that the water quality is adversely affected by anthropogenic activities, especially that the concentrations of N and P species are higher than they would naturally be. The seasonal pattern observed in the N and P time series indicates significant anthropogenic distortion of the natural biogeochemical cycles within the river. In a natural system, N and P concentrations would be expected to be at their lowest in the summer months when biological activity within the catchment and in the river is at its greatest (e.g., [73]), but the Enborne is showing the reverse pattern, which is typical of many rural lowland rivers (e.g., [31,74]). This suggests that temperature-dependent biological uptake is not controlling the seasonal nutrient dynamics as it does in more natural systems (e.g., [73]), but that delivery of nutrients to the river is driving the observed dynamics, with maximum concentrations occurring when flow, and thus dilution capacity, is at its lowest.

Determining the relative importance of sources of anthropogenic N and P in the river is more problematic. In terms of inputs to the catchment, agricultural fertiliser is overwhelmingly the dominant source of annual loads (Table 6). Moreover, the vast majority of this fertiliser is applied in March, April and May [49], and this period sees a marked increase in river N and P concentrations in both study years (Figure 4). On the other hand, this period is also the transition between the high flow, high dilution capacity and low flow, low dilution capacity regimes (Figure 4a), so the increase could be related to poorer dilution of point source inputs, such as from STWs. There is more evidence which suggests that STWs are an important source of both N and P. SRP dominates the P fractions composition of the Enborne, and is also the predominant species released from the STWs (Table 3). Transfer of P from agricultural land tends to be predominantly PP. SRP has previously been shown to correlate well with effluent markers and population density [45], and this is also observable in the Enborne with a strong significant correlation identified between SRP and boron (B) (Table 8).

Results reported by Wade *et al.* [38] demonstrated that a two-peak diurnal cycle could be observed within the Brimpton flow, TRP and NO_3 time series during periods of low flow, and these have been highlighted again here. Diurnal fluctuations in streamflow are common in natural river systems and are caused by diurnal changes in factors such as evapotranspiration and loss of water to the streambed (e.g., [75]). However, the occurrence of a two-peak diurnal cycle at low flows has been linked to STW discharges, which can exhibit two peaks each day linked to periods of greater domestic water consumption in the morning and evening [24,69,70]. As discussed in Wade *et al.* [38] 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. The finding of a two-peak diurnal cycle in the Enborne was unexpected as it is a rural catchment with a low population density by the standards of southeast England. The catchment STWs, however, provide a significant proportion of the water in the river at low flows (Figure 7, Section 4.5). Moreover, the two-peak diurnal signal in both P and N was still detectable at Brimpton even though it had advected down 16 km of river from the largest STW (Figure 1). Therefore, other inputs of P and N, dispersion and diffusion, and in-stream processing were not enough to erase the signal.

In addition to the STWs, there is a high density of STSs in the catchment. We estimate that at least 38% of the population is not connected to the sewage system (Sections 2.2 and 3.2), and that there are about 2760 domestic STSs. Of these, only 163 (6%) are officially registered, hence it is difficult to predict their effects. STSs can individually have the same characteristics as STWs, but on a smaller and less efficient scale. Their outputs will however have a variety of travel times to the river monitoring point, so would not be expected to give a clear signal in the same way as STWs. Much will also depend on how the STS soakaway connects to the river system. Of the 163 registered consented discharges, 78 connect directly to a watercourse, but the proportion is unlikely to be as high overall (until recently, a direct connection was the main reason for registration). Directly-connected STSs would be expected to have more effect on watercourses than those where the water soaks away to groundwater, which would be expected to remove much of the P and some of the N. Recent research has demonstrated the significance of septic tank discharges on the quality of river systems and processes of in-stream P and N cycling [33–35,76], but more information about them is needed in order to assess their effects. The significant contribution of STS and STW discharges to flows also has important implications when considering the future water quality of the systems as the increasing pressures of urbanisation, abstraction and climatic variability further alter the balance between STW discharges and river flows [21,67,77].

The mass balance (Table 6) shows that only 4% of the P inputs to the catchment, and 9% of the N inputs, leave in the river water. In order to understand what controls these outputs, and thus river concentrations, process understanding and the ability to model a complex web of interactions are required. STWs clearly have an effect on P and N concentrations in the Enborne which is out of proportion to their relatively modest contribution to nutrient inputs. In part this is because of their direct connection to the river compared to other sources, but there may be other reasons. We intend to explore this topic further using the high-frequency data.

5.2. Compliance with Legislative Targets

The current official ecological status of the Enborne under the WFD is “moderate” or “good” dependent on the reach. Of the three physico-chemical criteria, the Enborne comfortably meets the “good” WFD requirement for pH, with the 5th percentile of the dataset 7.6 and the 95th percentile 8.4, well within the permitted pH range of 6.0 to 9.0. For dissolved oxygen the system is also meeting the standard for “high” ecological status with the 10th percentile for the period of record equalling 72% saturation, 2% above the required saturation level. Despite these high dissolved oxygen levels, diurnal fluctuations as large as 90% can be observed within the high-frequency time series, with dramatic shifts in the diurnal range of oxygen levels at the onset of riparian shading. For example between the 22 and the 28 of April 2010, the range of dissolved oxygen saturation was 75 percentage points (82% to 157%), whereas for the following week this was only 31 percentage points (82% to 113%). For P, the standard for “good” is not being met, with the weekly samples giving a mean annual value of 0.13 mg P L^{-1} for SRP as opposed to 0.12 mg P^{-1}. The high-frequency data show that TRP concentrations were above 0.14 mg P L^{-1} for all of June, July and August in both 2010 and 2011. This is significant as these are the periods of lowest flow and therefore greatest residence time, highest temperatures, and high insolation, giving a greater risk of eutrophication, which is one effect the standard is supposed to protect against. So although the Enborne almost meets certain WFD standards for “good” status, as implemented in the UK, it can hardly be said to be in an ecologically-resilient state. This paper shows that both diffuse and point sources of P need to be tackled to improve the catchment status in relation to WFD targets; a finding consistent with other recent work in the wider Thames catchment [67].

6. Conclusions

The combination of high-frequency and conventional monitoring used in this paper has shown that it is possible to infer a great deal about the influences on lowland water quality in a 2-year campaign. The high-frequency data highlighted a complexity in nutrient dynamics which could never have been anticipated based on standard low-frequency monitoring, such as the two-peak diurnal cycle indicating sewage works influence. By monitoring for two years it has been possible to evaluate how these dynamics vary on a seasonal basis, with diurnal dynamics strongest across all determinands in the low flow periods of the spring and summer. More inferences can be made by examining these periods in more detail, and subsequent papers will explore these aspects further. However, calibrating and maintaining the field monitoring equipment is a major task, requiring trained technical staff, and both capital and running costs of such equipment are high. There is a need for cheaper, more robust high-frequency monitoring systems which can preferably run without mains power. But the present work shows that a lot can be learnt using current instrumentation, and also that the influences on water quality in UK lowland rivers will require further investigation.

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Conflicts of Interest

The authors declare no conflict of interest.

References

1. Office of National Statistics, National Population Projections: 2010-Based Statistical Bulletin. Available online: http://www.ons.gov.UK/ons/dcp171778_235886.pdf (accessed on 28 October 2013).
2. Bronstert, A. Rainfall-runoff modelling for assessing impacts of climate and land-use change. *Hydrol. Processes* **2004**, *18*, 567–570.
3. Johnson, A.C.; Acreman, M.C.; Dunbar, M.J.; Feist, S.W.; Giacomello, A.M.; Gozlan, R.E.; Hinsley, S.A.; Ibbotson, A.T.; Jarvie, H.P.; Jones, J.I.; *et al.* The British river of the future: How climate change and human activity might affect two contrasting river ecosystems in England. *Sci. Total Environ.* **2009**, *407*, 4787–4798.
4. Limbrick, K.J.; Whitehead, P.G.; Butterfield, D.; Reynard, N. Assessing the potential impacts of various climate change scenarios on the hydrological regime of the River Kennet at Theale, Bberkshire, south-central England, UK: An application and evaluation of the new semi-distributed model, INCA. *Sci. Total Environ.* **2000**, *251*, 539–555.
5. Hulme, M.; Jenkins, G.J.; Lu, X.; Turnpenny, J.R.; Mitchell, T.D.; Jones, R.G.; Lowe, J.; Murphy, J.M.; Hassell, D.; Boorman, P.; *et al. Climate Change Scenarios for the United Kingdom: The UKCIP02 Scientific Report*; Tyndall Centre for Climate Change Research, School of Environmental Sciences, University of East Anglia: Norwich, UK, 2002; p. 120.
6. Brown, R.; Acheson, R. *The Climate is Changing—Time to Get Ready*; Environment Agency: Bristol, UK, 2005; p. 32. Available online: http://www.direct.gov.UK/prod_consum_dg/ groups/dg_digitalassets/@dg/@en/documents/digitalasset/dg_073021.pdf (accessed on 28 October 2013).
7. Environment Agency. *Water for People and the Environment—Water Resources Strategy: Regional Strategy Actions for South East Region*; Environment Agency: Reading, UK, 2012; p. 32. Available online: http://www.environment-agency.gov.UK/static/documents/Research/120327_WRStrategy_Regional_strategy_actions_FINAL.pdf (accessed on 28 October 2013).
8. Marsh, T. The 2004–2006 drought in southern Britain. *Weather* **2007**, *62*, 191–196.
9. Marsh, T.; Cole, G.; Wilby, R. Major droughts in England and Wales, 1800–2006. *Weather* **2007**, *62*, 87–93.
10. BBC, Cumbrian Floods 2009. *BBC News Cumbria*, 7 December 2009. Available online: http://news.bbc.co.UK/local/cumbria/hi/people_and_places/newsid_8378000/8378388.stm (accessed on 28 October 2013).
11. Hannaford, J. UK Flooding—Briefing from the Centre for Ecology & Hydrology—20 November 2009. Available online: http://www.ceh.ac.UK/news/news_archive/2009_news_item_48.html (accessed on 28 October 2013).

12. Withers, P.J.A.; Haygarth, P.M. Agriculture, phosphorus and eutrophication: A European perspective. *Soil Use Manag.* **2007**, *23*, 1–4.
13. Haygarth, P.M.; Condron, L.M.; Heathwaite, A.L.; Turner, B.L.; Harris, G.P. The phosphorus transfer continuum: Linking source to impact with an interdisciplinary and multi-scaled approach. *Sci. Total Environ.* **2005**, *344*, 5–14.
14. Durand, P.; Breuer, L.; Johnes, P.J. Nitrogen Processes in Aquatic Ecosystems. In *European Nitrogen Assessmen*; Sutton, M.A., Howard, C.M., Erisman, J.W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H., Grizzetti, B., Eds.; Cambridge University Press: Cambridge, UK, 2011; pp. 126–146.
15. Beven, K. Towards integrated environmental models of everywhere: Uncertainty, data and modelling as a learning process. *Hydrol. Earth Syst. Sci.* **2007**, *11*, 460–467.
16. Wilby, R.L.; Whitehead, P.G.; Wade, A.J.; Butterfield, D.; Davis, R.J.; Watts, G. Integrated modelling of climate change impacts on water resources and quality in a lowland catchment: River Kennet, UK. *J. Hydrol.* **2006**, *330*, 204–220.
17. Naddeo, V.; Zarra, T.; Belgiorno, V. Optimization of sampling frequency for river water quality assessment according to italian implementation of the EU Water Framework Directive. *Environ. Sci. Policy* **2007**, *10*, 243–249.
18. Environment Agency (EA). *Water Resources in England and Wales—Current State and Future Pressures*; EA: Bristol, UK, 2008; p. 22. Available online: http://cdn.environment-agency.gov.UK/geho1208bpas-e-e.pdf (accessed on 28 October 2013).
19. Environment Agency. Creating a Better Place 2010–2015: Our Corporate Strategy. Available online: http://www.letsrecycle.com/resources/doc/news/2009/Corporate_Strategy.pdf (accessed on 28 October 2013).
20. Burns, J. UK Rivers Failing New EU Standard. *BBC News*, 23 November 2009. Available online: http://news.bbc.co.UK/1/mobile/sci/tech/8267686.stm (accessed on 28 October 2013).
21. Neal, C.; Jarvie, H.P.; Wade, A.J.; Whitehead, P.G. Water quality functioning of lowland permeable catchments: Inferences from an intensive study of the River Kennet and upper River Thames. *Sci. Total Environ.* **2002**, *282*, 471–490.
22. Lischeid, G.; Bittersohl, J. Tracing biogeochemical processes in stream water and groundwater using non-linear statistics. *J. Hydrol.* **2008**, *357*, 11–28.
23. Jordan, P.; Arnscheidt, J.; McGrogan, H.; McCormick, S. High-resolution phosphorus transfers at the catchment scale: The hidden importance of non-storm transfers. *Hydrol. Earth Syst. Sci.* **2005**, *9*, 685–691.
24. Palmer-Felgate, E.J.; Jarvie, H.P.; Williams, R.J.; Mortimer, R.J.G.; Loewenthal, M.; Neal, C. Phosphorus dynamics and productivity in a sewage-impacted lowland chalk stream. *J. Hydrol.* **2008**, *351*, 87–97.
25. Jarvie, H.P.; Sharpley, A.N.; Withers, P.J.A.; Scott, J.T.; Haggard, B.E.; Neal, C. Phosphorus mitigation to control river eutrophication: Murky waters, inconvenient truths, and “postnormal” science. *J. Environ. Qual.* **2013**, *42*, 295–304.
26. Jarvie, H.P.; Neal, C.; Withers, P.J.A. Sewage-effluent phosphorus: A greater risk to river eutrophication than agricultural phosphorus? *Sci. Total Environ.* **2006**, *360*, 246–253.

27. Bowes, M.J.; Smith, J.T.; Jarvie, H.P.; Neal, C. Modelling of phosphorus inputs to rivers from diffuse and point sources. *Sci. Total Environ.* **2008**, *395*, 125–138.
28. Neal, C.; Martin, E.; Neal, M.; Hallett, J.; Wickham, H.D.; Harman, S.A.; Armstrong, L.K.; Bowes, M.J.; Wade, A.J.; Keay, D. Sewage effluent clean-up reduces phosphorus but not phytoplankton in lowland chalk stream (River Kennet, UK) impacted by water mixing from adjacent canal. *Sci. Total Environ.* **2010**, *408*, 5306–5316.
29. Bowes, M.J.; Smith, J.T.; Neal, C. The value of high-resolution nutrient monitoring: A case study of the River Frome, Dorset, UK. *J. Hydrol.* **2009**, *378*, 82–96.
30. Jarvie, H.P.; Sharpley, A.N.; Scott, J.T.; Haggard, B.E.; Bowes, M.J.; Massey, L.B. Within-river phosphorus retention: Accounting for a missing piece in the watershed phosphorus puzzle. *Environ. Sci. Technol.* **2012**, *46*, 13284–13292.
31. Bowes, M.J.; Leach, D.V.; House, W.A. Seasonal nutrient dynamics in a chalk stream: The River Frome, Dorset, UK. *Sci. Total Environ.* **2005**, *336*, 225–241.
32. Tesoriero, A.J.; Duff, J.H.; Saad, D.A.; Spahr, N.E.; Wolock, D.M. Vulnerability of streams to legacy nitrate sources. *Environ. Sci. Technol.* **2013**, *47*, 3623–3629.
33. Macintosh, K.A.; Jordan, P.; Cassidy, R.; Arnscheidt, J.; Ward, C. Low flow water quality in rivers; septic tank systems and high-resolution phosphorus signals. *Sci. Total Environ.* **2011**, *412*, 58–65.
34. Withers, P.J.A.; Jarvie, H.P.; Stoate, C. Quantifying the impact of septic tank systems on eutrophication risk in rural headwaters. *Environ. Int.* **2011**, *37*, 644–653.
35. May, L.; Place, C.; O'Malley, M.; Spears, B. *The Impact of Phosphorus Inputs from Small Discharges on Designated Freshwater Sites*, CEH Project Number: C03655; NERC—Centre for Ecology and Hydrology, Natural England and Broads Authority: Edinburgh, UK, 2011; p. 130.
36. Neal, C.; Jarvie, H.P.; Withers, P.J.A.; Whitton, B.A.; Neal, M. The strategic significance of wastewater sources to pollutant phosphorus levels in english rivers and to environmental management for rural, agricultural and urban catchments. *Sci. Total Environ.* **2010**, *408*, 1485–1500.
37. LIMPIDS. Linking Improved Modelling of Pollution to Innovative Development of Sensors. Available online: http://www2.hull.ac.uk/science/envmon/limpids.aspx (accessed on 28 October 2013).
38. Wade, A.J.; Palmer-Felgate, E.J.; Halliday, S.J.; Skeffington, R.A.; Loewenthal, M.; Jarvie, H.P.; Bowes, M.J.; Greenway, G.M.; Haswell, S.J.; Bell, I.M.; *et al*. Hydrochemical processes in lowland rivers: Insights from *in situ*, high-resolution monitoring. *Hydrol. Earth Syst. Sci.* **2012**, *16*, 4323–4342.
39. Yellow Springs Instruments (YSI). Environmental Monitoring Systems Operations Manual: 6–Series Multi-Parameter Water Quality Sondes User Manual. Available online: http://www.ysi.com/index.php (accessed on 28 October 2013).
40. Murphy, J.; Riley, J.P. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* **1962**, *27*, 31–36.
41. Systea. On Line Analyser for Potable Surface Water and Waste Water Monitoring. Available online: http://www.systea.it/ (accessed on 28 October 2013).

42. Hach-Lange. *Nitratax—User Manual*; Hach Lange Ltd.: Manchester, UK, 2007; Volume DOC023.54.03211. Available online: http://www.hach.com/asset-get.download-en.jsa?id=7639982966 (accessed on 28 October 2013).
43. Bowes, M.J.; Gozzard, E.; Johnson, A.C.; Scarlett, P.M.; Roberts, C.; Read, D.S.; Armstrong, L.K.; Harman, S.; Wickham, H. Spatial and temporal changes in chlorophyll-a concentrations in the River Thames basin, UK: Are phosphorus concentrations beginning to limit phytoplankton biomass? *Sci. Total Environ.* **2012**, *426*, 45–55.
44. Neal, C.; Skeffington, R.; Neal, M.; Wyatt, R.; Wickham, H.; Hill, L.; Hewitt, N. Rainfall and runoff water quality of the Pang and Lambourn, tributaries of the River Thames, south-eastern England. *Hydrol. Earth Syst. Sci.* **2004**, *8*, 601–613.
45. Neal, C.; Bowes, M.; Jarvie, H.P.; Scholefield, P.; Leeks, G.; Neal, M.; Rowland, P.; Wickham, H.; Harman, S.; Armstrong, L.; *et al*. Lowland river water quality: A new UK data resource for process and environmental management analysis. *Hydrol. Processes* **2012**, *26*, 949–960.
46. Office of National Statistics, Neighborhood Statistics—2011 Census Data. Available online: http://www.neighbourhood.statistics.gov.uk (accessed on 28 October 2013).
47. EDiNA & DEFRA. Edina Agcensus Database. EDiNA at Edinburgh University Data Library and DEFRA. Available online: http://edina.ac.uk/agcensus/ (accessed on 28 October 2013).
48. Morton, D.; Rowland, C.; Wood, C.; Meek, L.; Marston, C.; Smith, G.; Wadsworth, R.; Simpson, I.C. *Final Report for LCM2007—The New UK Land Cover Map*, CEH Project Number: C03259; Countryside Survey Technical Report No.11/07; NERC/Centre for Ecology & Hydrology: Lancaster, UK, 2011; p. 112.
49. DEFRA. British Survey of Fertiliser Practice. Available online: https://www.gov.uk/government/collections/fertiliser-usage (accessed on 28 October 2013).
50. DEFRA. UK Atmospheric Deposition Data. Available online: http://pollutantdeposition.defra.gov.UK/data (accessed on 28 October 2013).
51. Neal, C.; Jarvie, H.P.; Wade, A.J.; Neal, M.; Wyatt, R.; Wickham, H.; Hill, L.; Hewitt, N. The water quality of the locar pang and lambourn catchments. *Hydrol. Earth Syst. Sci.* **2004**, *8*, 614–635.
52. UK Meteorological Office. *Met Office Integrated Data Archive System (Midas) Land and Marine Surface Stations Data (1853-Current)*; NCAS British Atmospheric Data Centre: Didcot, UK, 2013. Available online: http://badc.nerc.ac.uk/view/badc.nerc.ac.uk__ATOM__dataent_ukmo-midas (accessed on 28 October 2013).
53. Thames Water. Sewage Treatment Work Data for Works within the Thames Water Region, Personal Communitcation, 2013.
54. DEFRA. Sewage Treatment in the UK: UK Implementation of the EC Urban Waste Water Treatment Directive. Available online: http://archive.defra.gov.uk/environment/quality/water/waterquality/sewage/uwwtd/documents/uwwtreport2.pdf (accessed on 28 October 2013).
55. Walling, D.E.; Webb, B.W. Estimating the discharge of contaminants to coastal waters by rivers: Some cautionary comments. *Mar. Pollut. Bull.* **1985**, *16*, 488–492.
56. Littlewood, I.G.; Marsh, T.J. Annual freshwater river mass loads from Great Britain, 1975–1994: Estimation algorithm, database and monitoring network issues. *J. Hydrol.* **2005**, *304*, 221–237.

57. Johnes, P.J. Uncertainties in annual riverine phosphorus load estimation: Impact of load estimation methodology, sampling frequency, baseflow index and catchment population density. *J. Hydrol.* **2007**, *332*, 241–258.
58. Jolliff, J.K.; Kindle, J.C.; Shulman, I.; Penta, B.; Friedrichs, M.A.M.; Helber, R.; Arnone, R.A. Summary diagrams for coupled hydrodynamic-ecosystem model skill assessment. *J. Mar. Syst.* **2009**, *76*, 64–82.
59. Marsh, T.J.; Hannaford, J. *UK Hydrometric Register—Hydrological Data UK Series*; Centre for Ecology & Hydrology: Wallingford, UK, 2008; p. 210.
60. Hampshire Biodiversity Partnership. Water and Biodiversity—Topic Action Plan—July 2003. Available online: http://www.hampshirebiodiversity.org.uk/pdf/PublishedPlans/Water_BAP.pdf (accessed on 28 October 2013).
61. Natural England. Site of Special Scientific Interest Database. Available online: http://www.sssi.naturalEngland.org.UK/Special/sssi/search.cfm (accessed on 28 October 2013).
62. Evans, D.J.; Johnes, P. Physico-chemical controls on phosphorus cycling in two lowland streams. Part 1—The water column. *Sci. Total Environ.* **2004**, *329*, 145–163.
63. Evans, D.J.; Johnes, P.J.; Lawrence, D.S. Physico-chemical controls on phosphorus cycling in two lowland streams. Part 2—The sediment phase. *Sci. Total Environ.* **2004**, *329*, 165–182.
64. Environment Agency. The Kennet and Pang Catchment Abstraction Management Strategy—2004. Available online: http://a0768b4a8a31e106d8b0-50dc802554eb38a24458b98ff72d550b.r19.cf3.rackcdn.com/geth0404bhxh-e-e.pdf (accessed on 28 October 2013).
65. Environment Agency. Database of Consented Discharges to Controlled Waters with Conditions—England and Wales. Available online: http://www.geostore.com/environment-agency/WebStore?xml=environment-agency/xml/dataLayers_CDCWC.xml (accessed on 28 October 2013).
66. UK Technical Advisory Group WFD. UK Environmental Standards and Conditions Report (Phase 1)—Final Report—2008. Available online: http://www.wfdUK.org/resources%20/UK-environmental-standards-and-conditions-report-phase-1 (accessed on 28 October 2013).
67. Whitehead, P.G.; Crossman, J.; Balana, B.B.; Futter, M.N.; Comber, S.; Jin, L.; Skuras, D.; Wade, A.J.; Bowes, M.J.; Read, D.S. A cost-effectiveness analysis of water security and water quality: Impacts of climate and land-use change on the River Thames system. *Philos. Trans. R. Soc. A* **2013**, *371*, doi:10.1098/rsta.2012.0413.
68. Jackson, B.M.; Wheater, H.S.; Mathias, S.A.; McIntyre, N.; Butler, A.P. A simple model of variable residence time flow and nutrient transport in the chalk. *J. Hydrol.* **2006**, *330*, 221–234.
69. Food and Agriculture Organization (FAO) of the United Nations. *Wastewater Treatment and Use in Agriculture*; FAO: Rome, Italy, 1992; p. 125. Available online: http://www.fao.org/docrep/t0551e/t0551e00.HTM (accessed on 28 October 2013).
70. Withers, P.J.A.; Jarvie, H.P. Delivery and cycling of phosphorus in rivers: A review. *Sci. Total Environ.* **2008**, *400*, 379–395.
71. Loperfido, J.V.; Just, C.L.; Papanicolaou, A.N.; Schnoor, J.L. *In situ* sensing to understand diel turbidity cycles, suspended solids, and nutrient transport in Clear Creek, Iowa. *Water Resour. Res.* **2010**, *46*, doi:10.1029/2009WR008293.
72. Nimick, D.A.; Gammons, C.H.; Parker, S.R. Diel biogeochemical processes and their effect on the aqueous chemistry of streams: A review. *Chem. Geol.* **2011**, *283*, 3–17.

73. Halliday, S.J.; Skeffington, R.A.; Wade, A.J.; Neal, C.; Reynolds, B.; Norris, D.; Kirchner, J.W. Upland streamwater nitrate dynamics across decadal to sub-daily timescales: A case study of Plynlimon, Wales. *Biogeosci. Discuss.* **2013**, *10*, 13129–13189.
74. Jarvie, H.P.; Withers, P.J.A.; Bowes, M.J.; Palmer-Felgate, E.J.; Harper, D.M.; Wasiak, K.; Wasiak, P.; Hodgkinson, R.A.; Bates, A.; Stoate, C.; *et al*. Streamwater phosphorus and nitrogen across a gradient in rural–agricultural land use intensity. *Agric. Ecosyst. Environ.* **2010**, *135*, 238–252.
75. Lundquist, J.D.; Cayan, D.R. Seasonal and spatial patterns in diurnal cycles in streamflow in the western United States. *J. Hydrometeorol.* **2002**, *3*, 591–603.
76. Palmer-Felgate, E.J.; Mortimer, R.J.G.; Krom, M.D.; Jarvie, H.P. Impact of point-source pollution on phosphorus and nitrogen cycling in stream-bed sediments. *Environ. Sci. Technol.* **2010**, *44*, 908–914.
77. Wade, A.J.; Hornberger, G.M.; Whitehead, P.G.; Jarvie, H.P.; Flynn, N. On modeling the mechanisms that control in-stream phosphorus, macrophyte, and epiphyte dynamics: An assessment of a new model using general sensitivity analysis. *Water Resour. Res.* **2001**, *37*, 2777–2792.