Article (refereed) - postprint

Bowes, Michael J.; Jarvie, Helen P.; Naden, Pamela S.; Old, Gareth H.; Scarlett, Peter M.; Roberts, Colin; Armstrong, Linda K.; Harman, Sarah A.; Wickham, Heather D.; Collins, Adrian L. 2014. **Identifying priorities for nutrient mitigation using river concentration-flow relationships: the Thames basin, UK.**

Identifying priorities for nutrient mitigation using river concentration-flow relationships: the Thames basin, UK

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Key words

Phosphorus; Nitrogen; Load Apportionment Model; Thames Initiative; point source; diffuse source.

Abstract

The introduction of tertiary treatment to many of the sewage treatment works (STW) across the Thames basin in southern England has resulted in major reductions in river phosphorus (P) concentrations. Despite this, excessive phytoplankton growth is still a problem in the River Thames and many of its tributaries. There is an urgent need to determine if future resources should focus on P removal from the remaining STW, or on reducing agricultural inputs, to improve ecological status. Nutrient concentration-flow relationships for monitoring sites along the River Thames and 15 of its major tributaries were used to estimate the relative inputs of phosphorus and nitrogen from continuous (sewage point sources) and rain-related (diffuse and within-channel) sources, using the Load Apportionment Model (LAM). The model showed that diffuse sources and remobilisation of within-

channel phosphorus contributed the majority of the annual P load at all monitoring sites. However, the majority of rivers in the Thames basin are still dominated by STW P inputs during the ecologically-sensitive spring-autumn growing season. Therefore, further STW improvements would be the most effective way of improving water quality and ecological status along the length of the River Thames, and 12 of the 15 tributaries. The LAM outputs were in agreement with other indicators of sewage input, such as sewered population density, phosphorus speciation and boron concentration. The majority of N inputs were from diffuse sources, and LAM suggests that introducing mitigation measures to reduce inputs from agriculture and groundwater would be most appropriate for all but one monitoring site in this study. The utilisation of nutrient concentration-flow data and LAM provide a simple, rapid and effective screening tool for determining nutrient sources and most effective mitigation options.

1 Introduction

Significant amounts of expenditure and resources are currently being focussed on reducing phosphorus (P) and nitrogen (N) inputs to UK rivers (Pretty et al., 2003), to mitigate the ecological problems associated with eutrophication, achieve good ecological status, and comply with the European Union's Water Framework Directive (2000). The principle methods of achieving this are through improved nutrient removal at sewage treatment works (STW) and the control of diffuse (non-point) inputs from agriculture, through source controls (e.g., rate, method and timing of applied nutrients) and transport controls (e.g., conservation tillage, contour ploughing and riparian buffer strips). These sorts of mitigation measures have been incentivised through agri-environment schemes, and, in some circumstances, regulated e.g. via Cross Compliance expectations of farmers and restrictions on certain land management practices, such as in designated Nitrate Vulnerable Zones as part of the EU Nitrate Directive (Collins et al., 2007).

Many of the rivers of the Thames basin in southern England have seen dramatic reductions in phosphorus concentrations since the late 1990s, due primarily to the introduction of phosphorus removal across a range of STW, including the 36 largest STW serving populations of over 10,000 (Kinniburgh and Barnett, 2010). This has resulted in *ca*. 90% reduction in soluble reactive phosphorus concentrations in the River Thames (Bowes et al., 2012b; Kinniburgh and Barnett, 2010) and many of its tributaries (Jarvie et al., 2006a; Jarvie et al., 2002; Neal et al., 2010a). Despite these step reductions in phosphorus concentrations, there is little evidence that eutrophication risk has been reduced. Indeed, many parts of the Thames basin (particularly the lower Thames and its tributaries, the River Kennet, Ray and Thame) still suffer from excessive phytoplankton biomass (Bowes et al., 2012a) and nutrient limitation experiments on the River Thames and River Kennet have shown that P and N concentrations are still in excess for periphyton growth (Bowes et al., 2012b; Bowes et al., 2010a). Therefore, there is a pressing need to identify the most effective and appropriate nutrient mitigation measures for each of the wide range of rivers within the Thames Basin. For example, would it now be most effective to introduce P removal at the smaller, rural STW, or to focus most of the resources into reducing diffuse agricultural inputs? The key to answering this question is to determine the relative contributions of nutrient coming from sewage and agriculture for each individual river (Withers and Sharpley, 2008), particularly during the environmentally-sensitive spring to autumn growing period (Jarvie et al., 2006b).

A wide range of nutrient source apportionment methodologies already exist and are routinely applied to rivers by both catchment managers and researchers. Many are GIS-based land use models (Bowes et al., 2005a; Johnes et al., 1996; May et al., 2001). These source-orientated approaches can provide useful estimates of point and diffuse loads, but they are usually not based on catchment-specific empirical data, and they often have an annual timestep, which means that they are unable to provide source quantification during the growing season. Load-orientated approaches, such as the Environment Agency's SIMCAT model (Crabtree et al., 2009), quantify diffuse nutrient load by subtracting the estimated point inputs from the measured river load (EEA, 2005). This approach is useful in estimating changes in water quality along a river continuum, but within-channel nutrient retention processes (Bowes and House, 2001) could greatly underestimate diffuse source contributions. A new, simple and effective method of nutrient source apportionment; the Load Apportionment Model, has been developed in recent years (Bowes et al., 2010b; Bowes et al., 2008; Bowes et al., 2009; Chen et al., 2013; Greene et al., 2011; Howden et al., 2009; Jarvie et al., 2010), based on routinely monitored nutrient concentration and river volumetric flow data. The model uses the differences in the timing and flow–dependence of point and diffuse inputs, to quantify their relative source contributions. The majority of point inputs of phosphorus and nitrogen to UK rivers will be from STW effluents, and these will be relatively constant from day to day, and largely independent of rainfall. Therefore, rivers dominated by STW inputs of P and N will have highest concentrations during periods of low flow, and this concentration will decrease reciprocally with increasing river flow, due to dilution. Conversely, rivers that receive nutrients primarily from diffuse, rainfall–related inputs will tend to show an increase in nutrient load and/or concentration with increasing river flow, due to the nutrient inputs being concomitant with runoff from agricultural land during storm events (Arnscheidt et al., 2007; Jarvie et al., 2006b; Jordan et al., 2007; Neal et al., 2000d; Wood et al., 2005).

The aim of this study was to use the relationships between the nutrient concentration and flow data, gathered over two years from multiple river sites across the Thames basin, as a rapid screening tool to infer the relative inputs from constant (sewage) and rain-related (diffuse and within-channel remobilised) sources. The Load Apportionment Model (LAM) was used to quantify these inputs. These model outputs were assessed, alongside the seasonality of these nutrient inputs, to identify the best management option for reducing P and N inputs for each individual river, and improving ecological status / reducing excessive algal growth in the future.

2 Methodology

2.1 Catchment description

The River Thames extends 354 km from its source in the Cotswold Hills, Gloucestershire, to its tidal limit at Teddington, south west London, covering a catchment area of 9948 km^2 (Marsh and Hannaford, 2008). The Thames basin contains the UK's capital, London, and other major urban centres, including Swindon, Oxford, Slough and Reading (Figure 1). Despite the catchment's relatively high human population density (ca. 960 people km^{-2}) (Merrett, 2007), much of the upper and western River Thames basin is relatively rural (Environment_Agency, 2009), with ca. 45 % of land area being classified as arable, 11 % woodland, 34 % grassland, and only 6% urban / semi-urban development (Fuller et al., 2002). The catchment is predominantly underlain by Cretaceous Chalk geology, with areas of impermeable clays in the River Enborne, Ray and Thame sub-catchments, and Oolitic Limestones in the upper catchment. Mean annual rainfall in the mid Thames basin (near Oxford) was 745 mm (Marsh and Hannaford, 2008). This study focuses on the Thames basin from Hannington Wick in the upper catchment to Runnymede, near Slough, just upstream of the tidal limit (Figure 1). Catchment areas, land cover and STW population equivalents (PE) upstream of each water quality monitoring site were determined in ARC GIS using the Centre for Ecology and Hydrology's (CEH) Intelligent River Network (Dawson et al., 2002), the

CEH Land Cover Map 2000 (Fuller et al., 2002), using the RACQUEL web application (Table 1). This shows the great variety of sub-catchments within the basin, ranging from the predominantly-rural River Leach, Pang and Lambourn (with STW population equivalent densities of $\leq$ 30 km^{-2} and <5% urban / semi-urban land cover) to rivers that are predominantly urban receiving extremely high STW effluent loadings, such as The Cut, River Wye and the upper River Thames at Hannington, with STW PE of over 400 km^{-2}.

2.2 Sampling and water quality analysis

Water quality samples were taken at weekly intervals from six monitoring sites along the River Thames, and from fifteen of its major tributaries, as part of the Centre for Ecology and Hydrology's (CEH) Thames Initiative research platform and the CEH Lambourn Observatory research site. Sampling began in February 2009 at 18 of the monitoring sites, and a further three sites (River Enborne, River Kennet and the River Thames at Hannington) were added to the monitoring programme in late 2009. This monitoring is ongoing, and this paper presents data up until the end of May 2011. Most monitoring sites were located at or near Environment Agency flow gauging stations, to provide high-quality river discharge data. The river discharges at monitoring sites that were not at gauging stations were modelled, based on nearby gauging station data from that river, corrected by the difference in catchment area (Bowes et al., 2012a).

Bulk water samples were taken from the main river flow of each monitoring site. Sub-samples were filtered through a 0.45 μm cellulose nitrate membrane (WCN grade: Whatman, Maidstone, UK) in the field, for determination of soluble reactive phosphorus (SRP), nitrate, nitrite, ammonium, total dissolved nitrogen and boron concentrations. An unfiltered sub-sample was taken for total phosphorus (TP) analysis. On return to the laboratory, the samples were stored at $4^{o}C$ in the dark. Total phosphorus was determined by acid digestion and molybdate colorimetry (Eisenreich et al., 1975). SRP concentrations were determined by the phosphomolybdenum blue colorimetry method of Murphy and Riley (1962), as modified by Neal et al., (2000b) (Auto Analyser 3; Seal Analytical, Fareham, UK). Samples were analysed within 24 hours, to minimise errors associated with sample instability(House and Warwick, 1998). Nitrate and nitrite concentration was analysed by ion chromatography (Dionex DX500; Sunnyvale, California, USA). Ammonium (NH_4^+) concentration was determined using an indophenol-blue colorimetric method (Leeks et al., 1997) (Auto Analyser 3; Seal Analytical, Fareham, UK). Total dissolved nitrogen was determined by thermal oxidation and chemoluminescence of a filtered water sample (Total Nitrogen Analyser, Analytical Sciences, Cambridge, UK). Boron concentrations were measured by inductively-coupled plasma optical emission spectroscopy (Perkin Elmer Optima 2100). Further information on the analytical methods used can be found in Neal et al., (2000c).

2.3 Load apportionment modelling

LAM uses the fundamental differences in the P concentration-flow relationship to estimate the relative nutrient contributions from continuous and flow-related sources.

A full description of how the model operates is given elsewhere (Bowes et al., 2008; Bowes et al., 2009). In brief, the phosphorus concentration, C_p (mg m^{-3}) at the monitoring point can be expressed as:

$$C_p = A.Q^{B-1} + C.Q^{D-1} \tag{1}$$

where Q (m^3 s^{-1}) is the volumetric flow rate of the river, and *A*, *B*, *C* and *D* are load coefficients to be determined empirically. The $A.Q^{B-1}$ term is the nutrient concentration originating from ‘constant’ (i.e. non flow-related) sources, which, in most catchments in Britain, will equate to point sources, particularly sewage effluent from STW and septic tank misconnections. The $C.Q^{D-1}$ term in Equation 1 is the nutrient concentration originating from rainfall and flow-related sources, and will largely equate with diffuse source inputs derived from agriculture, groundwater, road run-off and septic tank soak-aways. This rain-related signal will also include combined sewer overflows from STW, and the remobilisation of within-channel material (stored within the bed-sediment and river biota) that is transported during periods of increased river flows. Much of this remobilised within-channel nutrient could have originated from STW inputs during low flow periods, and this source could be a significant proportion of the rain-related phosphorus signal, particularly for rivers with relatively low velocities and large quantities of fine bed sediments, which are typical of the Thames catchment.

The four load coefficients in Equation (1) were determined (using the *Solver* function in Microsoft EXCEL©) to provide the closest fit to the empirical P concentration and flow data. To provide realistic solutions, *D* was forced to be greater than 1 (diffuse nutrient load inputs must increase with increasing flow). To simplify the modelling within this study, the *B* term (representing within-channel retention and remobilisation processes acting on constant inputs) was not used, and was set to zero during the modelling stage. The effects of varying the *A*, *C* and *D* load coefficients on the nutrient concentration / flow relationships are shown in Figure 2, along with an example (for the River Cole) of how the model fits the empirical concentration and flow data (Figure 2 (d)). The model solution is the sum of the constant source contribution (derived from the *A* load coefficient) added to the rain-related source contribution (derived from the *C* and *D* terms). The point at which the estimated constant and flow-dependent inputs were equal (Q_e, $m^3\ s^{-1}$) (Figure 2(d)) was calculated by:

$$Q_e = \left(\frac{A}{C}\right)^{\left(1/(D-B)\right)} \qquad (2)$$

This Q_e value was then used to determine the percentage of time where constant, non-flow-related nutrient sources were the major contributor to the total nutrient inputs throughout the monitoring period (i.e. what percentage of time was the river flow less than the Q_e value). This Q_e value of a river can be key in evaluating the most appropriate and effective means of improving ecological quality and reducing nutrient concentrations during the algal growing season.

Once the LAM had been successfully calibrated to the empirical data for a river site, this nutrient concentration/flow relationship was then applied to the daily mean river flow data set for the monitoring period, to calculate the total annual phosphorus load T_p (mg yr^{-1}):

$$T_p = 86400.\sum_{i=1}^{i=365} A.Q_i^B + C.Q_i^D \tag{3}$$

where Q_i is the mean daily volumetric flow rate (m^3 s^{-1}), A, C and D are the empirically-determined load coefficients from Equation (1), and 86,400 is the number of seconds in one day. Equation (3) consists of both a constant source ($A.Q_i^B$) and a flow-related source ($C.Q_i^D$) term. Therefore, the results of the model fitting can be used to determine the proportion of the total annual nutrient load that is contributed individually by constant (equating to point sewage inputs) and flow-dependent (equating to diffuse inputs and remobilised within-channel load) nutrient sources.

3 Results and discussion

3.1 Water quality data

The mean nutrient concentrations for each of the 21 monitoring sites observed during the study period are shown in Table 2. The monitoring sites covered a wide range of nutrient enrichment, with mean

SRP concentrations varying from 17 to 571 µg l^{-1}. The lowest phosphorus concentrations (SRP < 40 µg l^{-1}) were observed in the relatively rural tributaries; the Rivers Leach, Pang, Lambourn and Kennet. The Rivers Pang, Leach and Lambourn also have the lowest STW population equivalent densities of ≤30 km^{-2} (Table 1). The River Kennet had a higher population density connected to the sewerage system (115 STW PE km^{-2}), but had much lower SRP concentrations than sites with similar STW PE densities, such as the River Windrush (128 STW PE km^{-2}; mean SRP = 74 µg l^{-1}) and River Evenlode (94 STW PE km^{-2}; mean SRP = 157 µg l^{-1}). The River Kennet is designated as a Site of Special Scientific Interest (SSSI), which has meant that all significant STW discharging into the River Kennet have tertiary phosphorus removal treatment installed (Neal et al., 2010b). This potentially demonstrates the water quality that could be achieved if the use of P removal technology was extended to smaller rural STW across the rest of the Thames basin.

The highest mean SRP and TP concentrations were observed in the urbanised tributaries of The Cut, the River Thame and River Ray, which receive effluent from major STW serving the towns of Bracknell (PE = 74600), Aylesbury ((PE = 94400) and Bicester (PE = 39860) respectively. These high-phosphorus concentration sites had between 73 and 83 % of the TP load in SRP form, which suggests they are receiving high sewage effluent loading (Millier and Hooda, 2011). (On average in the UK, approximately 70 % of the TP load in STW final effluent is in SRP form (Jarvie et al., 2006b)). The sites with the lowest proportion of the phosphorus load in SRP form were the Rivers Kennet (39 %), Pang (53 %) and Leach (55 %), again suggesting low sewage effluent inputs and a predominance of particulate P input from agricultural, diffuse sources. Mean phosphorus concentrations along the River Thames itself remained relatively constant at *ca.* 200 µg l^{-1}, indicating that either P inputs were regular and consistent along the river continuum (which they clearly are, due to the dense distribution of STW within the catchment), or that P concentrations were being mediated by retention and release processes between the water column and within-channel sediment / biota.

The River Thames and most of its tributaries had relatively high mean total dissolved nitrogen concentrations of between 5.8 and 8 mg l^{-1} (Table 2). Over 90% of this TDN is in the form of nitrate at all monitoring sites. High nitrate concentrations are commonly observed in groundwater-dominated Chalk catchments across southern England (Bowes et al., 2011; Neal et al., 2012), due to a legacy of manure and fertiliser pollution linked to agricultural intensification (Howden et al., 2010; Smith et al., 2010). The River Enborne and River Cole had lower TDN concentrations of 4.4 and 5.0 mg l^{-1}, respectively, which may be due to their clay drift geology reducing their connectivity with nitrate-enriched groundwaters. The base flow index values for these catchments were only 0.53 and 0.54 respectively, compared with 0.6 to 0.97 for the other monitoring sites (Marsh and Hannaford, 2008). The three monitoring sites with the highest mean TP and SRP concentrations (the River Ray, River Thame and The Cut) also had the highest nitrogen concentrations, with TDN concentrations of 8.5, 9.2 and 21.6 mg N l^{-1} respectively. They also had the highest ammonium concentrations (between 0.9 and 2.0 % of TDN). This combination of high TP and TDN concentrations, with high proportions of SRP and ammonium, indicate these most highly nutrient-polluted sites are dominated by sewage effluent inputs. This conclusion is further supported by the high STW PE densities within these catchments (Table 1) and the high mean boron concentrations (a constituent of detergents, and therefore a sewage tracer (Neal et al., 2005)), which are indicative of a strong sewage effluent signal (Table 2).

3.2 Nutrient concentration – flow relationships

3.2.1 Phosphorus

All six River Thames monitoring sites exhibited a dilution of TP concentration with increasing river discharge at low flows, and then an increase in TP concentration at higher river discharge (Figure 3). Very similar relationships were also observed with the SRP concentrations at these sites (data provided in Supplementary Information). This implies that there is both a strong constant phosphorus input and a rain-related source at higher flow rates (equating to diffuse inputs and remobilisation of within-channel P), reflecting the mixed land use of dense urbanisation with large areas of intensive agriculture that typifies the Thames basin. The constant phosphorus inputs will primarily equate to STW point source inputs to the River Thames, but will also include some groundwater inputs, although these will be relatively small. P concentrations in Thames basin groundwaters are low (<20 μg l^{-1}) due to P precipitation within the Chalk geology (Neal et al., 2002; Sorensen et al., 2013). The patterns in the phosphorus concentration-flow relationship had a lot of scatter, especially at intermediate flows, indicating either the presence of intermittent phosphorus pollution events that were neither constant nor rain-related (Jordan et al., 2007), or there were large hysteresis patterns during some storm events. Unfortunately the relatively low frequency (weekly) monitoring programme employed in this study is not suitable for investigating these hysteresis effects further.

The LAM solutions and estimated contributions from constant and rain-related sources are given in Table 3, and the Q_e values are shown in Figure 3. Due to the hysteresis / scatter in the P concentration-flow relationship, the LAM was unable to produce realistic fits to the data for three of the River Thames sites at Newbridge, Swinford and Wallingford. The optimal model solution was to plot a horizontal line through the data at the average TP concentration, which was unrealistic, as it assumed that there were no constant inputs (despite there being a clear dilution of TP concentration at low flows) and a constant concentration sourced from the rain-related component. Therefore, weightings were applied to mean TP concentrations at low, median and high flows for these sites, to produce more believable, sub-optimal solutions for these sites. Despite this, the model appears to have underestimated the constant source component, as shown by the position of the Q_e values not coinciding with the break-point in the TP concentration – flow relationship for the sites at Newbridge, Swinford and Wallingford. This also applies to the River Thames at Hannington Wick (Figure 3).

Despite the 90 % reduction in phosphorus concentrations due to STW improvements since the late 1990s, the LAM still estimates that over 20 % of the remaining TP load is derived from constant sources in the mid to lower River Thames, and these constant STW inputs contribute the majority of the load for over 50% of the year in the lower Thames (Table 3).

Most of the tributary monitoring sites had much less scatter in the TP-flow relationship, compared with the River Thames sites (Figure 4). The River Kennet and Pang exhibited an increase in TP concentration with increasing flow, indicating a complete dominance of rain-related, diffuse sources.

However, it is clear that these rivers do receive some constant phosphorus inputs from the STWs within the catchments, and this must be being removed from the water column and stored within the river channel, due to sequestration by sediment or bioaccumulation by river biota (Bowes and House, 2001; Jarvie et al., 2012). The River Lambourn had a small constant-source dilution signal at low flow (Figure 4), but also appeared to be predominantly diffuse source dominated. These deductions were supported by both the water quality and GIS data, which shows that these three diffuse dominated rivers have the lowest boron concentrations (<22 µg l^{-1}), low proportion of TP in SRP form, low urban land covers (< 4.4 %) and relatively low STW PE densities. For all of the other tributaries, their highest observed TP concentrations occurred during low flow periods, and they displayed a marked dilution with increasing flow, indicating that constant, point source inputs must still contribute significantly to P status, despite the improvements to STW over the last decade.

The LAM produced realistic fits to the empirical data for 12 of the 15 tributary sites (Table 3). The model was unable to provide a fit to the monitoring data for the River Wye and Cherwell, due to the lack of a pattern in the TP concentration–flow relationship, and the River Windrush, probably due to significant hysteresis patterns causing scatter in the TP concentration–flow relationships. All tributary sites showed that the majority of the annual TP load was derived from rain-related sources (Table 3), varying from 100 % for the River Pang and Kennet, to ca. 60 to 70 % for the Rivers Colne, Cole, Evenlode, Ock, Enborne and Thame. However, TP at seven of the 12 tributary sites was dominated by constant sources for 50% or more of the time, showing that sewage inputs still dominated P loads for the majority of the year, and particularly during the summer low flow periods.

3.2.2 Nitrate

The nitrate concentration–flow relationships, with LAM solutions are shown in Figure 5. The majority of the monitoring sites showed increases in nitrate concentration with increasing river flow during low flow periods, and then a levelling off to a constant nitrate concentration at medium to high river flows. This may indicate that diffuse surface and near-surface nitrate inputs (e.g. from overland flow, soil leaching / through-flow, road runoff and field drains), and within-channel remobilisation, are most significant during low-flow rainfall events, but these sources become exhausted, and groundwater nitrate inputs dominated at medium to high river flow in all rivers. However, this pattern in the nitrate-flow relationship may also suggest that there are significant N losses through denitrification and biological uptake with decreasing flows during the growing season. Significant rates of within-channel N uptake of up to 30 % during the summer have been observed in mass-balance studies of other English chalk streams (Bowes et al., 2005b). Four of the high base-flow index rivers (the River Pang, Kennet, Windrush and Lambourn) had relatively constant nitrate concentrations, irrespective of river flow, indicating that these systems were dominated by groundwater nitrate inputs throughout the annual cycle, irrespective of rainfall. Another four of the 21 monitoring sites (the Rivers Thame, Enborne, Wye and the upper Thames at Hannington) showed decreases in nitrate concentration with increasing river discharge during low flow periods, indicating some significant constant-source inputs, but the nitrate load of these rivers became dominated by rain-related, diffuse sources at higher river flows. The Cut was the only monitoring site that produced a nitrate dilution curve across a full range of flows (Figure 5), indicating it was primarily impacted by constant-source STW-derived nitrogen. The Cut has the highest STW PE density of 1644 people km^2 (Table 1) and also has the lowest base flow index (0.46), indicating that it receives the least amount of nitrate-polluted groundwater. The LAM estimated that nitrate load at this site was predominantly derived from a constant (point) source for 73 % of the time, and contributed 44 % of the total nitrate load.

3.3 Selection of suitable mitigation measures

The principal aim of nutrient mitigation measures is to reduce phosphorus and nitrogen concentrations in rivers to limit excessive primary production, and thereby improve ecological status. As excessive algal and plant growth only occurs during the spring to autumn ‘growing period’ in temperate rivers, mitigation measures need to specifically target the reduction of nutrient concentrations during this environmentally sensitive period. The LAM’s daily timestep, and its ability to identify the flow at which diffuse and point source inputs are equal (Q_e) provides a valuable tool that enables us to explore the most suitable mitigation measures for each site.

3.3.1 Phosphorus

All of the River Thames monitoring sites clearly exhibit both constant and rain-related source signals in their P concentration – flow relationship, with dilution under low flow conditions and increasing P concentrations at higher flows. Load Apportionment modelling estimated that constant source inputs accounted for between 13 and 26% of the total phosphorus annual load, and so rain-related diffuse sources and within-channel remobilisation provided by far the greatest P load contribution (Table 3). Traditional source apportionment approaches, particularly those with an annual timestep, may use this information to recommend that diffuse mitigation measures would therefore be most effective for the Thames Catchment. However, the majority of the highest observed TP and SRP concentrations during the March – September growing period for all the River Thames sites occurred at low flows, at river flows less than the LAM Q_e value (Figure 3, SRP data provided in Supplementary Information), when constant sources dominate. Therefore, the most effective way to reduce the risks associated with eutrophication and to improve ecological status along the length of the River Thames would be to further reduce point source STW inputs, as this would reduce P concentrations during the ecologically-sensitive growing period. Similar conclusions about the continuing need for STW P removal to comply with the WFD have been made in other modelling studies of the River Thames (Crossman et al., 2013; Whitehead et al., 2013) and other UK catchments (Crabtree et al., 2009).

Load Apportionment Modelling estimated that the majority of the annual P loads of all tributary monitoring sites were also derived from rain-related diffuse sources and within-channel remobilisation (Table 3). However, much of this load was transported during winter high-flow events, when there was no risk of excessive algal blooms and associated ecological damage. Seven of the tributaries (River Evenlode, Coln, Ock, Enborne, Cole, Cut and Thame) were point source dominated for the majority of the year, and these tributaries (plus the River Leach) had the majority of their high-P-concentration observations (during the growing season) at flows less than their LAM Qe flow values (Figure 4). Therefore, the ecological status of these sites would most likely to be improved by targeting constant STW inputs, rather than by introducing diffuse mitigation measures. The LAM was unable to find solutions for the River Windrush and Cherwell, and the model fit for the

River Ray was also questionable (as the *Qe* value seemed too low, by visual inspection). However, by merely examining the P concentration–flow relationship, there are clear point source dilution signals during March – September, and again, this would imply that it would be most effective to reduce STW inputs to these tributaries, as this would reduce P concentration during the growing season. The River Pang, Lambourn and Kennet exhibited little or no point source dilution at low flow, and had relatively consistent P concentrations across the full range of annual river flows (Figure 4). The majority (or all of) the March – September data points are at flows greater than the *Qe* for these monitoring sites. Therefore, diffuse source mitigation measures would be most appropriate for these three tributaries.

3.3.2 Nitrate

The majority of the annual nitrate loads at all monitoring sites in this study were dominated by diffuse sources (Table 3). Most sites had no detectable constant source signal, and only one tributary (The Cut) showed a dominance of constant source contribution during any part of the annual cycle. Twelve of the 21 monitoring sites (middle and lower Thames sites, and the River Coln, Cole, Leach, Evenlode, Cherwell and Ock) showed marked increases in nitrate concentrations with increasing flows, particularly at low flows (Figure 5). Therefore, mitigation measures that target the reduction of diffuse, rain-related N inputs should be employed within these catchments, to attempt to improve water quality. However, these low nitrate concentrations at low flows may also be due to denitrification or enhanced uptake by biota, and may actually indicate sites that have enhanced primary production due to eutrophication. The River Pang, Lambourn, Kennet and Windrush had relatively stable nitrate concentrations, irrespective of flow, which implied that nitrate inputs were largely derived from groundwater, rather than fast-flow-path diffuse inputs. Therefore, N mitigation measures that target the reduced contamination of groundwater may be the most appropriate for these catchments. However, due to the long residence times of groundwater in Chalk rivers, this mitigation is very unlikely to have any immediate impact. The three monitoring sites that showed highest nitrate concentrations at lowest flows (the upper River Thames at Hannington, and the Thame, and Enborne tributaries) would most benefit from either reductions in STW N inputs, or diffuse mitigation measures targeting reductions in N input during the March – September growing season.

The Cut was the only monitoring site that was point source dominated (Figure 5), and reducing N inputs from STW would be the most appropriate strategy to begin to improve the water quality for this tributary. However, this tributary is so grossly enriched with both N and P that major reductions in nutrient concentrations would be required before any ecosystem response would likely to be observed (Bowes et al., 2012b).

4 Conclusions

This study has shown that the majority of rivers in the Thames basin are still dominated by STW P inputs during the growing season, despite the major programme of STW improvements that have taken place across the catchment since the late 1990s. Further STW improvements would be the most effective way of improving water quality and ecological status along the length of the River Thames, and for most of its tributaries. The only exceptions (where diffuse mitigation measures would be most appropriate) were two of the predominantly rural catchments (River Pang and Lambourn) with STW PE densities of less than 30 PE km^{-2}, and the River Kennet, which has already had P stripping installed in all of its STW. The introduction of phosphorus stripping at STW would not only reduce P concentration at the ecologically sensitive time of year, but it would also reduce the proportion of the TP load in bioavailable SRP form, which would be less ecologically damaging (Millier and Hooda, 2011). In contrast, reducing the largely rain-related diffuse inputs may reduce annual load, but is unlikely to reduce P concentrations during the growing period. The introduction of further P stripping at STW would also reduce the rain-related ‘diffuse’ signal, as this signal is partially composed of remobilised within-channel P, and a significant proportion of this is likely to have originally been derived from STW inputs during low flow periods (Jarvie et al., 2012). More widely, there is increasing evidence that while agricultural diffuse-source mitigation programs have been very successful at reducing P losses in runoff at the edge-of-field, there has often been less marked improvement in downstream water quality at the catchment scale (Jarvie et al., 2013b). This may result from inadequate intensity and targeting of source and transport controls (Sharpley et al., 2009) and complex and lagged water quality responses over timescales of years, decades or longer (Meals et al., 2010; Osmond et al., 2012). These lags may be linked to the persistent and chronic release of diffuse-source signals from 'legacy P', which has accumulated in catchments, and can mask downstream water quality improvements (Jarvie et al., 2013a; Sharpley et al., 2013). In contrast, point source mitigation has had an almost immediate and dramatically impact on reducing P loads and concentrations in many rivers, including the rivers of the Thames basin (Bowes et al., 2011; Kelly and Wilson, 2004; Millier et al., 2010; Neal et al., 2000a).

The CEH Thames Initiative monitoring programme has shown that there is a wide range of average TP concentrations across the Thames catchment, ranging from 30 to 700 µg l^{-1}. P concentrations of less than 100 µg SRP l^{-1} have been shown to be potentially limiting for periphyton (Bowes et al., 2012b; Bowes et al., 2007), and therefore it is important that nutrient mitigation is focussed on rivers that are already below this threshold, or at sites where the proposed mitigation measures have a reasonable chance of reducing growing-season SRP concentrations to below 100µg l^{-1} so that an ecological improvement may be achieved. If a mitigation measure fails to reduce the P concentration to a potentially-limiting concentration, there is unlikely to be an ecological response, ecological status will not be improved, and the site will not comply with the WFD.

In contrast, the majority of N inputs to rivers across the Thames basin were from diffuse sources, and Load Apportionment modelling suggests that introducing mitigation measures to reduce inputs from agriculture and groundwater would be most appropriate for all but one monitoring site in this study. The exception was The Cut, which was dominated by STW inputs. All rivers monitored in this study were grossly polluted with nitrogen, with average nitrate concentrations varying between 4 and 20 mg l^{-1} NO_3-N. Reducing N concentrations down to potentially limiting levels will be extremely difficult, especially as the major N source to these rivers is the groundwater, which can have residence times of many decades in groundwater-dominated river systems (Sharpley et al., 2013; Smith et al., 2010).

The interpretation of nutrient concentration–flow relationships in rivers, and where clear relationships exist, application of the LAM, offers a simple and rapid screening tool for identifying nutrient sources within a catchment, using widely available environmental data. The source apportionment it produces is in close agreement with catchment GIS statistics (such as STW PE density), phosphorus and nitrogen chemical speciation, and boron sewage tracer concentrations. The high frequency temporal data the LAM produces makes it a valuable tool for selecting the most appropriate mitigation options, which is a vital step in focussing available resources on achieving WFD Good Ecological Status for rivers in the future.

Acknowledgements

The water quality monitoring data was produced as part of the Centre for Ecology and Hydrology's Thames Initiative research platform, which has been funded by the Natural Environment Research Council. The modelling was funded by Defra under WQ0223 (Developing a field tool kit for ecological targeting of agricultural diffuse pollution mitigation measures). Environment Agency river flow data was accessed via the CEH National River Flow Archive.

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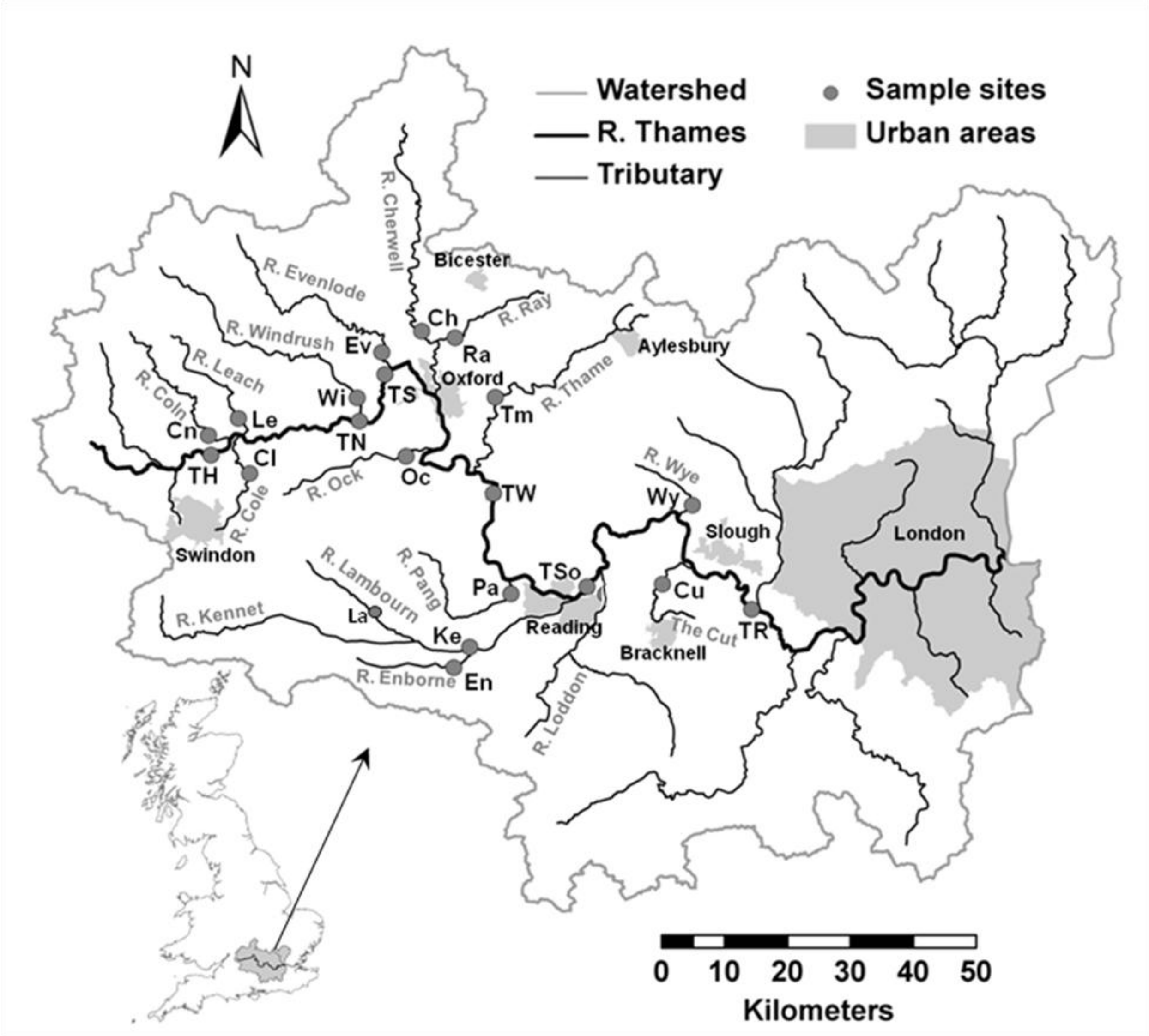
Figure 1



N
Watershed
R. Thames
Tributary
Sample sites
Urban areas
R. Cherwell
Bicester
R. Evenlode
R. Ray
Ch
Ra
R. Windrush
Ev
Aylesbury
R. Leach
Oxford
R. Coln
Wi
TS
Tm
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TH
Oc
R. Ock
TW
R. Wye
Wy
R. Cole
Slough
London
Swindon
R. Pang
R. Lambourn
TSo
Pa
Cu
R. Kennet
La
Reading
The Cut
TR
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Bracknell
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0 10 20 30 40 50
Kilometers

Figure 2

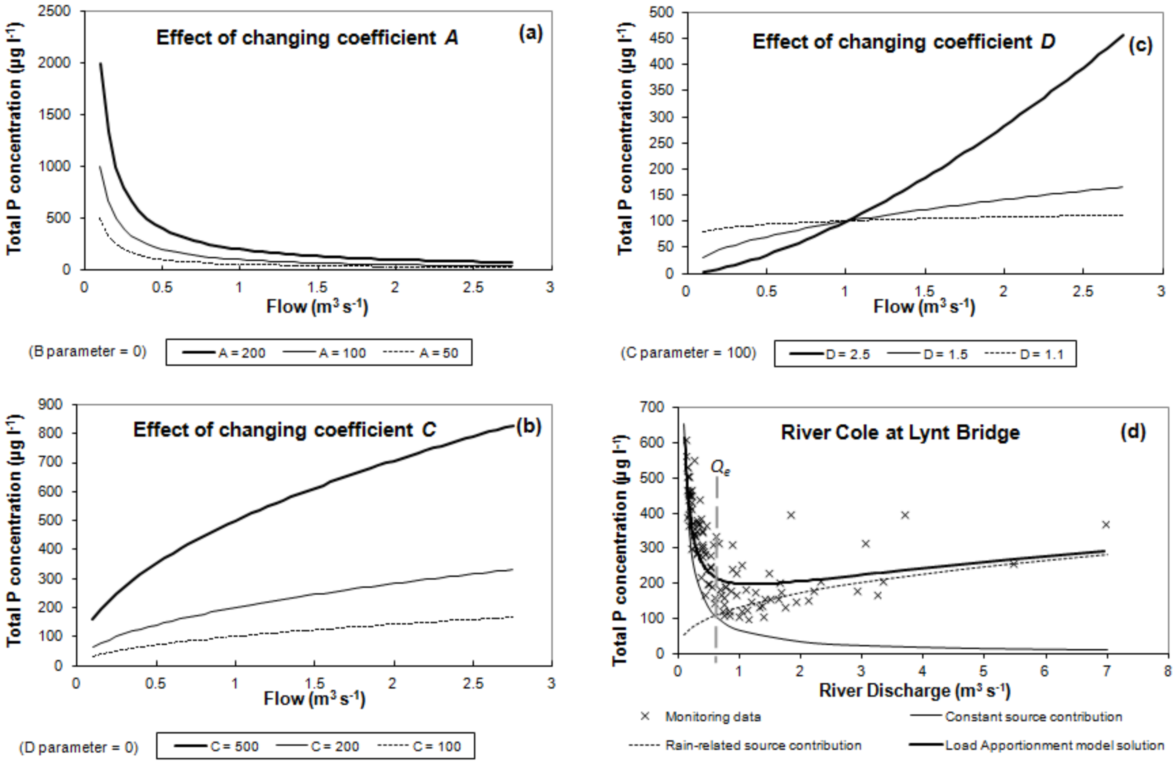
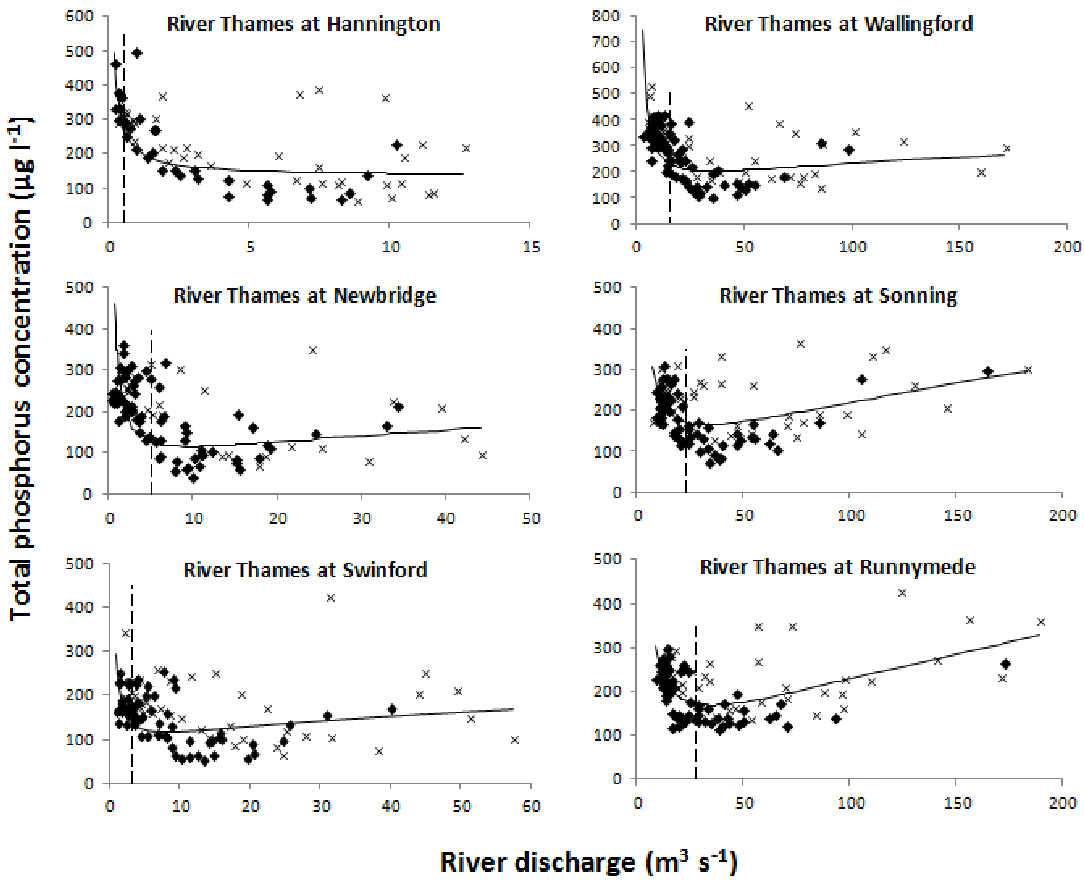

Effect of changing coefficient A
(a)
Total P concentration (µg l-1)
Flow (m3 s-1)
(B parameter = 0)
A = 200
A = 100
A = 50
Effect of changing coefficient D
(c)
(C parameter = 100)
D = 2.5
D = 1.5
D = 1.1
Effect of changing coefficient C
(b)
(D parameter = 0)
C = 500
C = 200
C = 100
River Cole at Lynt Bridge
(d)
Qe
River Discharge (m3 s-1)
Monitoring data
Constant source contribution
Rain-related source contribution
Load Apportionment model solution

Figure 3



River Thames at Hannington
River Thames at Wallingford
River Thames at Newbridge
River Thames at Sonning
River Thames at Swinford
River Thames at Runnymede
Total phosphorus concentration (µg l-1)
River discharge (m3 s-1)

Figure 4

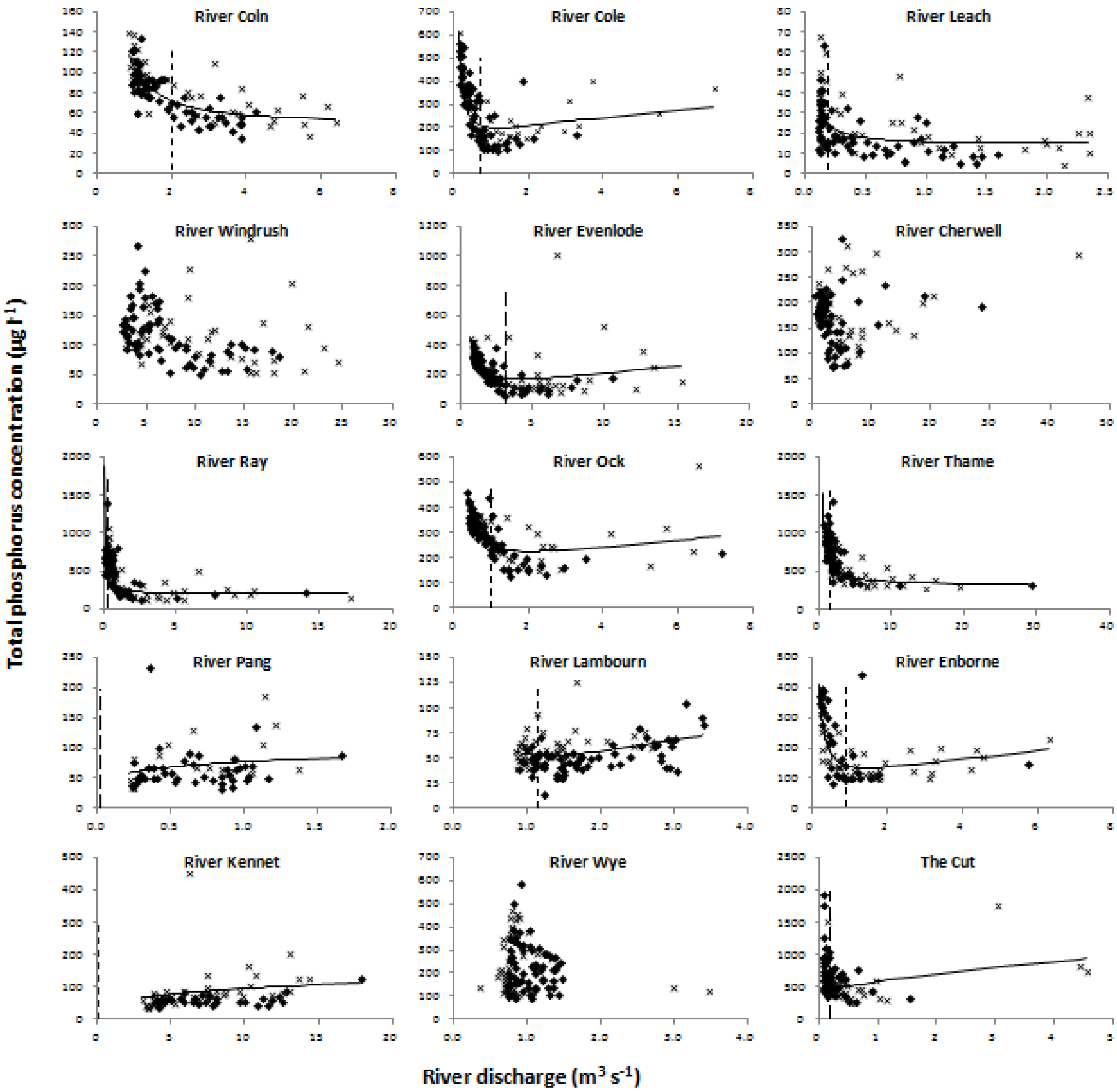

River Coln
River Cole
River Leach
River Windrush
River Evenlode
River Cherwell
River Ray
River Ock
River Thame
River Pang
River Lambourn
River Enborne
River Kennet
River Wye
The Cut
Total phosphorus concentration (μg l⁻¹)
River discharge (m³ s⁻¹)

Figure 5

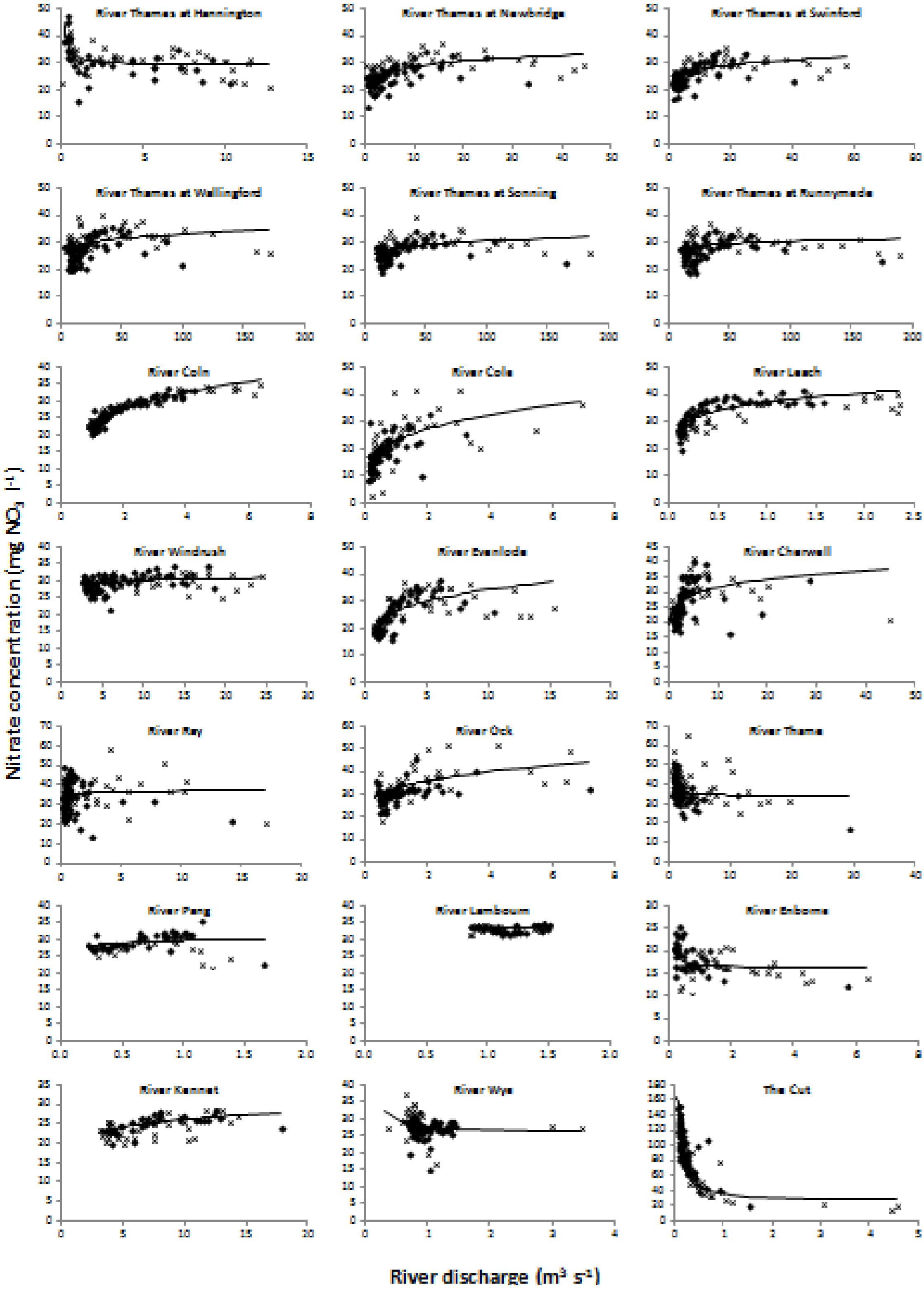

River Thames at Hannington
River Thames at Newbridge
River Thames at Swinford
River Thames at Wallingford
River Thames at Sonning
River Thames at Runnymede
River Coln
River Cole
River Leach
River Windrush
River Evenlode
River Cherwell
River Ray
River Ock
River Thame
River Pang
River Lambourn
River Enborne
River Kennet
River Wye
The Cut
Nitrate concentration (mg NO3 l-1)
River discharge (m3 s-1)

Table 1

Site code	River	Sampling site	Grid reference	Catchment area (km^2)	Distance to source (km)	% Land cover				Sewage treatment works population equivalent	STW population equivalent density (PE km^{-2})
						Woodland	Grassland	Arable	Urban / semi-urban		
TH	Thames	Hannington Wic	SU175961	567	47	10.9	40.5	38.3	8.2	237810	419
TN	Thames	Newbridge	SP403013	1229	78	10.0	35.3	45.7	7.2	290870	237
T Sw	Thames	Swinford	SP442085	1623	89	10.8	35.1	45.5	6.7	338300	209
TW	Thames	Wallingford	SU609902	4213	134	10.3	35.6	45.1	7.3	1027910	244
T So	Thames	Sonning	SU753758	5790	166	11.5	34.9	44.3	7.5	1586110	274
TR	Thames	Runnymede	TQ006723	7192	222	13.2	34.0	40.4	10.5	2661370	370
Cn	Coln	Whelford	SU171991	136	44	15.2	38.0	42.9	2.6	5440	40
Cl	Cole	Lynt Bridge	SU210980	141	29	7.2	35.9	42.0	13.1	6620	47
Le	Leach	Lechlade Mill	SU228996	77	29	9.7	22.8	64.2	2.0	1540	20
Wi	Windrush	Newbridge	SP403014	362	63	13.1	34.4	45.9	4.8	46300	128
Ev	Evenlode	Cassington Mill	SP447101	427	58	14.1	31.5	48.5	4.9	40100	94
Ch	Cherwell	Hampton Poyle	SP499152	566	69	9.1	33.3	50.4	6.4	112270	198
Ra	Ray	Islip	SP527139	290	32	11.3	40.1	42.6	5.3	46020	159
Oc	Ock	Abingdon	SU495967	255	33	8.0	33.0	51.0	7.3	36780	144
Tm	Thame	Wheatley	SP612050	532	53	9.7	32.4	35.7	8.3	153710	289
Pa	Pang	Tidmarsh	SU636747	175	28	17.6	27.6	46.0	4.1	4990	29
La	Lambourr	Boxford	SU429721	162	15	8.9	33.8	51.8	2.0	4790	30
En	Enborne	Brimpton	SU569649	142	26	24.0	38.0	28.9	6.5	11110	78
Ke	Kennet	Woolhampton	SU572667	842	71	13.2	30.0	48.7	4.4	96380	115
Wy	Wye	Bourne End	SU895866	134	17	19.3	35.9	23.6	20.5	82300	613
Cu	The Cut	Paley Street	SU869762	63	20	20.8	32.7	9.8	35.3	103600	1644

Table 2

Site code	River	Sampling site	Sampling period	Mean concentrations during sampling period							Mean flow ($m^3 s^{-1}$)
				Soluble reactive phosphorus ($\mu g\ l^{-1}$)	Total phosphorus ($\mu g\ l^{-1}$)	Nitrate-N ($mg\ l^{-1}$)	Nitrite-N ($mg\ l^{-1}$)	Ammonium-N ($mg\ l^{-1}$)	Total dissolved nitrogen ($mg\ N\ l^{-1}$)	Boron ($\mu g\ l^{-1}$)	
TH	Thames	Hannington Wi	September 2009 - April 2011	158	226	7.18	0.027	0.076	7.68	63	4.0
TN	Thames	Newbridge	February 2009 - April 2011	142	194	6.07	0.019	0.040	6.45	55	8.4
T Sw	Thames	Swinford	February 2009 - April 2011	107	160	6.07	0.016	0.036	6.43	48	11.2
TW	Thames	Wallingford	February 2009 - April 2011	192	282	6.66	0.023	0.050	7.14	78	30.2
T So	Thames	Sonning	February 2009 - April 2011	135	201	6.28	0.024	0.051	6.71	59	36.6
TR	Thames	Runnymede	February 2009 - April 2011	135	207	6.48	0.022	0.059	6.95	62	46.8
Cn	Coln	Whelford	February 2009 - April 2011	56	82	6.14	0.018	0.035	6.33	21	2.1
Cl	Cole	Lynt Bridge	February 2009 - April 2011	218	290	4.52	0.019	0.038	4.97	56	0.86
Le	Leach	Lechlade Mill	February 2009 - April 2011	17	31	7.41	0.026	0.044	7.63	25	0.59
Wi	Windrush	Newbridge	February 2009 - April 2011	74	118	6.73	0.014	0.022	6.97	34	3.0
Ev	Evenlode	Cassington Mil	February 2009 - April 2011	157	234	5.94	0.019	0.036	6.26	50	3.3
Ch	Cherwell	Hampton Poyle	February 2009 - April 2011	108	178	6.16	0.013	0.029	6.61	73	4.4
Ra	Ray	Islip	February 2009 - April 2011	385	466	7.84	0.040	0.078	8.54	110	1.7
Oc	Ock	Abingdon	February 2009 - April 2011	236	291	7.36	0.025	0.051	7.76	62	1.3
Tm	Thame	Wheatley	February 2009 - April 2011	571	700	8.49	0.040	0.187	9.23	89	3.1
Pa	Pang	Tidmarsh	February 2009 - April 2011	36	68	6.53	0.011	0.031	6.72	21	0.57
La	Lambourn	Boxford	February 2009 - April 2011	38	58	7.70	0.018	0.041	7.80	15	1.6
En	Enborne	Brimpton	November 2009 - April 2011	127	196	3.97	0.016	0.063	4.42	27	1.2
Ke	Kennet	Woolhampton	November 2009 - April 2011	31	80	5.62	0.017	0.030	5.87	22	7.3
Wy	Wye	Bourne End	February 2009 - April 2011	174	236	6.32	0.023	0.051	6.67	36	0.95
Cu	The Cut	Paley Street	February 2009 - April 2011	477	649	19.94	0.124	0.213	21.60	99	0.37

Table 3

Monitoring site		Total phosphorus						Nitrate					
River	Site	Model load coefficients			Constant source load	*Qe*	Time constant source dominated	Model load coefficients			Constant source load	*Qe*	Time constant source dominated
		A	C	D	(% of total load)	($m^3 s^{-1}$)	(%)	A	C	D	(% of total load)	($m^3 s^{-1}$)	(%)
Thames	Hannington Wick	70	159	1.0	13	0.4	13	3.37	29	1.0	3	0.12	0
Thames	Newbridge	318	31	1.4	22	5.1	25	0.16	23	1.1	0.1	0.01	0
Thames	Swinford	228	46	1.3	12	3.4	12	0	22	1.1	0	0	0
Thames	Wallingford	4806	585	1.0	26	8.2	39	0	24	1.1	0	0	0
Thames	Sonning	1978	14	1.6	21	23	51	0	22	1.1	0	0	0
Thames	Runnymede	2395	9	1.7	22	28	55	0	25	1.0	0	0	0
Coln	Whelford	72	32	1.2	43	2	61	0	23	1.2	0	0	0
Cole	Lynt Bridge	65	133	1.4	32	0.6	57	0	23	1.3	0	0	0
Leach	Lechlade Mill	2.4	13	1.1	23	0.2	39	0	37	1.1	0	0	0
Windrush	Newbridge				No model solution			0	28	1.0	0	0	0
Evenlode	Cassington Mill	269	42	1.6	40	3.1	64	0	22	1.2	0	0	0
Cherwell	Hampton Poyle				No model solution			0	24	1.1	0	0	0
Ray	Islip	50	200	1.0	11	0.3	16	0	35	1.0	0	0	0
Ock	Abingdon	127	123	1.4	33	1.0	59	0.79	31	1.2	1	0.04	0
Thame	Wheatley	450	320	1.0	32	1.4	50	4.90	34	1.0	5	0.15	0
Pang	Tidmarsh	0	77	1.2	0	0	0	0	30	1.0	0	0	0
Lambourn	Boxford	30	24	1.8	26	1.1	33	2.38	31	1.0	4	0.10	0
Enborne	Brimpton	64	74	1.5	32	0.9	58	0.73	16	1.0	4	0.04	0
Kennet	Woolhampton	0	48	1.3	0	0	0	0	20	1.1	0	0	0
Wye	Bourne End				No model solution			2.64	25	1.0	9	0.11	0
The Cut	Paley Street	50	534	1.4	17	0.2	55	9.20	27	1.0	44	0.34	73