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Spatial and temporal changes in chlorophyll-*a* concentrations in the River Thames basin, UK: Are phosphorus concentrations beginning to limit phytoplankton biomass?

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Abstract

Chlorophyll-*a* and nutrient concentrations were monitored at weekly intervals across 21 river sites throughout the River Thames basin, southern England, between 2009 and 2011. Despite a 90% decrease in soluble reactive phosphorus (SRP) concentration of the lower River Thames since the 1990s, very large phytoplankton blooms still occur. Chlorophyll concentrations were highest in the mid and lower River Thames and the larger tributaries. Lowest chlorophyll concentrations were observed in the smaller tributaries, despite some having very high phosphorus concentrations of over 300 $\mu\text{g l}^{-1}$. There was a strong positive correlation between river length and mean chlorophyll concentration ($R^2 = 0.82$), and rivers connected to canals had ca. six times greater chlorophyll concentration than ‘natural’ rivers with similar phosphorus concentrations, indicating the importance that residence time has on determining phytoplankton biomass. Phosphorus concentration did have some influence, with phosphorus-enriched rivers having much larger phytoplankton blooms than nutrient-poor rivers of a similar length. Water quality improvements may now be capping chlorophyll

peaks in the Rivers Thames and Kennet, due to SRP depletion during the spring / early summer phytoplankton bloom period. Dissolved reactive silicon was also depleted to potentially-limiting concentrations for diatom growth in the River Thames during these phytoplankton blooms, but nitrate remained in excess for all rivers throughout the study period. Other potential mitigation measures, such as increasing riparian shading and reducing residence times by removing impoundments may be needed, alongside phosphorus mitigation, to reduce the magnitude of phytoplankton blooms in the future.

Key words: Nutrient; Algae; Phytoplankton; Water quality; River Thames; Eutrophication.

1 Introduction

The reduction of nutrient concentrations, and phosphorus concentrations in particular, is seen by catchment managers as a key requirement to deliver good ecological status in waterbodies. The links between the level of nutrient enrichment and algal biomass is well understood for lakes (Canfield, 1983; Vollenweider, 1968). However, the link between phosphorus concentration and algal growth is less clear for rivers and streams (Hilton et al., 2006; Van Nieuwenhuysse and Jones, 1996). Some studies have established strong correlations between phosphorus concentration and algal biomass across ranges of rivers, principally in North America (Chetelat et al., 2006; Van Nieuwenhuysse and Jones, 1996), and these relationships have been used to propose target phosphorus concentrations to control excessive algal growth (Chambers et al., 2011; Dodds et al., 1998). Significant reductions in chlorophyll concentrations (an indicator of phytoplankton biomass) have been observed following reductions in phosphorus concentrations of the River Rhine in The Netherlands and the Sacramento and San Joaquin rivers in California, USA (Van Nieuwenhuysse, 2007), which supports the hypothesis that phosphorus concentration is the key control of phytoplankton

biomass. Conversely, other studies have shown little relationship between river nutrient concentration and either phytoplankton or periphyton biomass (Bernhardt and Likens, 2004; Figueroa-Nieves et al., 2006; Lewis and McCutchan, 2010; Royer et al., 2008; Yang et al., 2008), and reductions in river phosphorus concentrations in recent years have not resulted in the expected reduction in chlorophyll concentrations (Desortova and Puncochar, 2011; Neal et al., 2006).

There are other physical and biological factors that can affect phytoplankton biomass. Chlorophyll concentrations have been shown to be closely related to residence time and catchment area in many rivers (Neal et al., 2006; Royer et al., 2008; Søballe and Kimmel, 1987). Recent studies have shown the key role that light levels play in determining algal growth rates (Bowes et al., 2012; Hutchins et al., 2010; Munn et al., 2010; Whalen and Benson, 2007). Food web interactions and grazing has also been shown to control riverine algal biomass (Sabater et al., 2008; Twiss et al., 2010).

The River Thames (southern England) has seen major improvements in its water quality since the late 1990s, due principally to improvements in wastewater treatment (Bowes et al., 2010b; Kinniburgh and Barnett, 2010; Neal et al., 2010a). The annual mean soluble reactive phosphorus (SRP) concentration has declined from ca. 1000 $\mu\text{g l}^{-1}$ in the late 1990s to ca. 200 $\mu\text{g l}^{-1}$ in the late 2000s in the middle reaches of the River Thames, but despite this, maximum chlorophyll concentrations in 2009 were similar in magnitude as those observed from the 1970s to the early 1990s (Bowes et al., 2012; Kinniburgh et al., 1997; Whitehead and Hornberger, 1984). Many of the tributaries of the River Thames have seen similar reductions in phosphorus loading, and it is unknown if this improvement in water quality has resulted in reductions in phytoplankton biomass.

This paper presents weekly chlorophyll-*a* and water quality data from a wide range of rivers across the River Thames basin. These were used to investigate the role that nutrient concentration plays in controlling phytoplankton biomass, both spatially (between rivers) and temporally, through each growing season. The hypothesis to be tested was that the magnitude of the maximum chlorophyll-*a* concentrations at each study site is correlated to its average phosphorus concentration. Other possible controls of phytoplankton biomass, such as the concentration of other macronutrients (nitrogen and silicon) and residence time were also investigated. The water quality data sets were also used to indicate if nutrient limitation (by phosphorus, nitrogen or silicon) was occurring at any of these sites during periods of high phytoplankton biomass.

1.1 Catchment description

The River Thames is the largest river wholly in England, with a total length of 354 km to its tidal limit at Teddington in south west London and a catchment area of 9948 km² (Marsh and Hannaford, 2008). The Thames basin contains the UK's capital, London, and other major urban centres, including Swindon, Oxford, Slough, Maidenhead and Reading (Figure 1). The basin has a human population density of ca. 960 people km⁻² (Merrett, 2007). Despite this high population density, much of the River Thames basin upstream of London is relatively rural (Environment Agency., 2009), with ca. 45 % of land area being classified as arable, 11 % woodland, 34 % grassland, and only 6% classed as urban / semi-urban development (Fuller et al., 2002).

The catchment is predominantly underlain by Cretaceous Chalk geology, with areas of impermeable clays in the Enborne, Thame, Ray and Lodden sub-catchments, and Oolitic

Limestones in the upper catchment. Mean annual rainfall in the lower (Maidenhead), mid (near Oxford) and upper (near the confluence with the River Colne) Thames basin (was 714 mm, 745 mm and 738 mm respectively (Marsh and Hannaford, 2008).

1.2 Study sites

Monitoring was carried out as part of the Centre for Ecology and Hydrology's Thames Initiative research platform. Sites were located on all 15 major tributaries joining the River Thames between Hannington Wick (site TH) in the upper Thames basin and Slough (on the outskirts of London), and also six sites along the main stem of the River Thames (Figure 1, Table 1). This provided coverage of a wide range of river types, in terms of water quality, flow, land use and sewage input, and covered the majority of the basin above the tidal limit. Most sites were located near to UK Environment Agency flow gauging stations, to provide high-resolution river discharge data. Sampling began in February 2009 at 18 of the study sites, and a further three sites were added to the monitoring programme in late 2009. This paper presents data up until July 2011, and therefore covers three annual algae blooms for most sites.

2 Methodology

2.1 Sampling and chemical analysis

Bulk water samples were taken at weekly interval from bridges, from the main flow of the river at each monitoring site. Sub-samples were immediately filtered through a 0.45 µm cellulose nitrate membrane (WCN grade: Whatman, Maidstone, UK) for subsequent SRP, nitrate and dissolved reactive silicon analysis. Unfiltered sub-samples were taken for chlorophyll-a and total phosphorus (TP). River water temperature was also recorded at the time of sampling.

On return to the laboratory, the samples were stored at 4°C in the dark. Chlorophyll-*a* samples were filtered and processed within 24-h. The 0.5 litre river water samples were passed through a GF/C grade filter paper (Whatman, Maidstone, UK), and pigment extracted overnight from the suspended solid residue using 90 % acetone. The chlorophyll-*a* concentration of the extract was then determined spectrophotometrically (Marker et al., 1980). Total phosphorus (TP) was determined by digesting an unfiltered water sample with acidified potassium persulphate in an autoclave at 121°C for 40 minutes, then reacting with acid ammonium molybdate reagent to produce a molybdenum-phosphorus complex. This intensely coloured compound was then quantified spectrophotometrically at 880 nm (Eisenreich et al., 1975). SRP concentration was determined on a filtered sample, using the phosphomolybdenum blue colorimetry method of Murphy and Riley (1962), as modified by Neal et al., (2000a). Samples were analysed within 24 hours, to minimise errors associated with sample instability (House and Warwick, 1998; Jarvie et al., 2002). (SRP is considered equivalent to bioavailable phosphorus (House, 2003)). Dissolved reactive silicon concentration (termed silicon throughout the remaining paper) was determined by reaction with acid ammonium molybdate, to form yellow molybdosilicic acids. These were then reduced using an acidified tin (II) chloride solution to form intensely coloured silicomolybdenum blues, which were quantified spectrophotometrically using a Descrete Analyser (Auto Analyser 2; Seal Analytical, Fareham, UK) (Mullin and Riley, 1955). Nitrate concentration was analysed by ion chromatography (Dionex DX500).

3 Results and discussion

3.1 Temporal changes in chlorophyll concentration

Typical temporal variations in chlorophyll-*a* concentration from across the Thames basin are shown in Figure 2. Sustained phytoplankton blooms occurred between March and July each year at almost all study sites. Similar seasonal patterns in phytoplankton biomass have been observed in other British rivers, such as the River Frome, Dorset (Bowes et al., 2011; House et al., 2001), the Humber basin (Bowes and House, 2001; Neal et al., 2006) and also in previous studies of the Thames basin (Kinniburgh and Barnett, 2010; Kinniburgh et al., 1997; Lack, 1971; Neal et al., 2006; Palmer-Felgate et al., 2008; Whitehead and Hornberger, 1984). Many of these studies have associated this spring / early summer phytoplankton bloom with a proliferation of diatom species, due to the concurrent dip in dissolved reactive silicon concentration. (Diatoms are unicellular algae that bioaccumulate dissolved silicon from the water column to produce a silicate cell wall called a frustule). In the larger rivers (e.g. mid and lower River Thames, River Thame), these blooms were sustained for much of this March to July period, whereas the smaller rivers (e.g. River Cole) had more distinct, shorter duration peaks in chlorophyll concentration. A second peak in chlorophyll concentration is also observed at a number of sites (e.g. River Thames at Wallingford, River Lodden, River Cole) in the late summer / early autumn period (August to October) (Figure 2). Again this has been observed in other British rivers, and again associated with diatom blooms (Bowes et al., 2009).

It is unclear why the phytoplankton blooms are not sustained through the July to August summer period at any of the monitoring sites (Figure 2), and chlorophyll-*a* concentrations remain very low through this period, when conditions seem ideal for algal growth. Water temperatures, nutrient concentrations, light intensity and day length are at their greatest and

low river flows result in long residence times (Figure 3). The decline in chlorophyll-*a* could be due to a phytoplankton community shift that is dominated by algae that have photosynthetic pigments other than chlorophyll-*a*. It could also be due to temperature limitation. Studies of the River Frome in Dorset, southern England showed that diatom growth rates (as indicated by depressed dissolved reactive silicon concentrations) declined when water temperatures reached 15 °C (Bowes et al., 2011). Data from this study infers a similar temperature limitation effect during summer in all rivers, with dissolved reactive silicon concentration dips and chlorophyll peaks suddenly ceasing when temperatures (ranging from 15 to 21°C across the study sites) are reached. Alternatively, the apparent decline in phytoplankton could be due to grazing / foodweb interactions, with predator populations increasing during the summer period, in response to the algal bloom.

The one exception to this regular seasonal pattern was the River Leach (the site with the lowest phosphorus concentrations within this study), which showed no increase in chlorophyll concentration through the spring to early summer periods, and only had intermittent chlorophyll peaks in the autumn / winter periods (Figure 2), some corresponding to high flow events. This implies that the phytoplankton biomass is negligible in this small, phosphorus-poor stream, and the benthic algal community dominates. This benthic biomass was probably released into the water column outside the growing period due to sloughing at higher water velocities, resulting in the observed chlorophyll peaks.

There was a distinct pattern in chlorophyll concentrations through the three algae growing seasons of this study. The monitoring period was characterized by high chlorophyll concentrations in the larger rivers in both 2009 and 2011, and relatively low chlorophyll concentrations in 2010 (Table 1; Figure 2). Almost all of the smaller tributary sites had their

largest annual peak in either 2009 or 2011 (except the Rivers Enborne and Coln), and many sites had a two-fold reduction in chlorophyll-*a* in 2010, compared to these maximum values observed in 2009 or 2011. Maximum chlorophyll concentrations in the mid to lower Thames sites (Wallingford, Sonning and Runnymede) for 2009 and 2011 reached ca. 300 $\mu\text{g l}^{-1}$ (Table 1), which were typical of values observed throughout the period 1980 to 1996 for the River Thames at Reading (Kinniburgh and Barnett, 2010; Kinniburgh et al., 1997) when maximum SRP concentrations in some years were $> 4000 \mu\text{g l}^{-1}$. Similar annual patterns were also observed in the upper River Thames at Newbridge, and the Rivers Cherwell and Cole (Figure 2). The smaller tributaries had much less year-to-year variation in maximum chlorophyll concentration.

The reasons for the significant contrast between the major phytoplankton blooms in 2009 and 2011, and much smaller bloom in 2010, is unclear. The maximum water temperature and river flows during the summer periods were similar across the three years (Figure 3). However, there were significant differences in river conditions during the spring period, when the phytoplankton bloom was at its height. At the beginning of May, water temperature in the lower River Thames (Runnymede) was 17.0 and 15.3°C in 2009 and 2011 respectively, but only 12.2°C in 2010. The river discharges were also significantly different at this time (25.7 and 20.3 $\text{m}^3 \text{s}^{-1}$ in 2009 and 2011 respectively, and 46.4 $\text{m}^3 \text{s}^{-1}$ in 2010). This suggests that major river phytoplankton blooms may result from warm spring periods (possibly related to high light levels), and low river flow velocities which will increase residence times and reduce scouring of benthic biofilms. Similar conclusions on the effect of river flow on phytoplankton biomass have been made in previous studies of the Rivers Thames and Kennet (Lack, 1971). Further studies need to be conducted over longer timescales to investigate this

potential relationship between chlorophyll concentrations and flow, temperature and light during this critical spring period.

3.2 Spatial pattern in chlorophyll concentrations

The largest average and maximum chlorophyll concentrations were observed in the mid and lower River Thames (from Newbridge to Runnymede), and the four tributaries in the mid Thames catchment around Oxford (the Rivers Cherwell, Ray, Evenlode and Thame) (Figure 4a). The sites with the lowest average and maximum chlorophyll concentrations are the relatively short tributaries of less than 30 km; the Rivers Wye, Pang, Leach and Enborne. The upper River Thames at Hannington Wick, and the Rivers Windrush and Lodden also had low phytoplankton biomass.

For the main stem of the River Thames, there was a general increase in chlorophyll concentration downstream for each study year, with the upper Thames at Hannington Wick always having the lowest chlorophyll concentration, and the Thames at Wallingford and Runnymede having the maximum concentrations (Table 1). Similar increases in plankton biomass along a river continuum have been observed in previous studies of the Sacramento River, USA (Greenberg, 1964) and the Seine, France (Garnier et al., 1995). This supports the theories of Hilton et al., (2006) and Neal et al., (2006) that the residence time of a waterbody is the dominant control on phytoplankton abundance. However, there was not a simple relationship between chlorophyll concentration and distance downstream along the River Thames, and the Thames sites at Swinford and Sonning both showed decreases in chlorophyll concentration, compared with the Thames monitoring sites directly upstream (Newbridge and Wallingford). The reduction in phytoplankton abundance between the monitoring sites at Wallingford and Sonning, and Newbridge and Swinford, are probably due to the input of

low-chlorophyll-concentration water from the tributaries joining the Thames (the Rivers Kennet and Pang, and the River Windrush, respectively) (Figure 4a).

3.3 Links between nutrient concentrations and phytoplankton biomass

The spatial distribution of soluble reactive phosphorus concentrations across the Thames basin are shown in Figure 4b. The highest average SRP concentrations ($>400 \mu\text{g l}^{-1}$) were observed in some of the tributaries of the mid and lower Thames basin; the Rivers Ray, Cut and Thame. These sites are closely associated with high sewage treatment works (STW) loadings from the towns of Bicester (population estimate of 31 600), Bracknell (population estimate of 71 600) and Aylesbury (population estimate of 88 900) respectively. The lowest SRP and TP concentrations were observed in the relatively rural sub-catchments of the upper Thames basin (the River Leach, Coln and Windrush), and the River Kennet and Pang, draining the south-western section of the basin. The Kennet and Pang sub-catchments are also relatively rural, but the Kennet sub-catchment contains a number of significant towns and their associated sewage treatment works. However, much of the River Kennet has been designated as a Site of Special Scientific Interest, due to its rare assemblages of flora and fauna, and has already introduced high levels of wastewater treatment and phosphate removal at all its significant STWs (Neal et al., 2010b). This demonstrates how comprehensive point and diffuse nutrient mitigation measures can significantly reduce phosphorus concentrations in UK rivers, and may indicate what is possible for the other tributaries in the Thames basin in the future.

Nitrate concentrations were high throughout the Thames basin, with most study sites having average concentrations between 23 and 37 $\text{mg l}^{-1} \text{NO}_3$ (Table 1). These high nitrate concentrations are probably due to the legacy of agricultural pollution that has contaminated the groundwater that provides most of the river flow to these Chalk and limestone rivers,

particularly during summer low flow periods. The lowest average nitrate concentrations were observed in the Rivers Cole and Enborne (19.5 and 17.1 mg l⁻¹ respectively), which are underlain by clay deposits, thereby reducing the transfer of nitrate pollution from the groundwater to the river. The Cut at Paley Street had over twice the NO₃ concentration of any other river within the study, with an average concentration of 86 mg l⁻¹ and a maximum value of 151 mg l⁻¹ NO₃. This extremely high nitrate loading is almost certainly derived from the major STW inputs to this relatively small river from Bracknell STW (population estimate of 71 600). The next highest nitrate concentrations were observed in the River Ray at Islip and the River Thames at Wheatley. Again, both of these rivers receive significant sewage effluent inputs, resulting in high levels of both nitrate and phosphorus enrichment.

There are few clear similarities between the spatial pattern of chlorophyll and nutrient concentrations (Figure 4). The sites with maximum chlorophyll concentrations above 200 mg l⁻¹ (the mid and lower River Thames and the River Cherwell) all have relatively modest (in the context of this study) SRP concentrations of between 109 and 201 µg l⁻¹ and nitrate concentrations of between 25 and 30 mg l⁻¹ NO₃. Some of the most heavily nutrient-enriched sites (the Rivers Ock, Cole, Wye and The Cut) have very low average chlorophyll concentrations of less than 10 µg l⁻¹. However, there are some correlations that imply that there is a link between phytoplankton biomass and nutrient concentration. The five sites with SRP and TP concentrations below 100 µg l⁻¹ (the River Leach, Kennet, Pang, Coln and Windrush) have some of the lowest average chlorophyll concentrations of less than 10 µg l⁻¹. SRP concentrations of between 60 and 100 µg l⁻¹ have been identified as being growth-limiting to benthic biofilms during in-stream mesocosm studies of UK chalk rivers (Bowes et al., 2012; Bowes et al., 2010a; Bowes et al., 2007), and therefore the relatively low P concentrations at these sites may be reducing phytoplankton biomass. Conversely, two of the

three most phosphorus-enriched tributaries, the River Thame and Ray, also have some of the highest maximum and average chlorophyll concentrations.

Despite some apparent links between chlorophyll and phosphorus enrichment described above, there is no simple correlation between the maximum chlorophyll concentration observed within the monitoring period and the average total phosphorus concentration at each study site (Figure 5) (R^2 of 0.004). However, there appears to be two distinct patterns within this relationship (Figure 5). The chlorophyll concentrations of sites on the middle and lower Thames, and the River Cherwell correlate closely with TP concentration (R^2 of 0.79), and have much higher phytoplankton biomass for a particular TP concentration than the remaining sites. These sites (plus the River Kennet) are all used extensively for boating, and are interconnected with adjacent canals, and also have extensive lock systems and weirs built into the river. These dead zones will greatly increase the residence time of the river water, and thereby allow time for the phytoplankton to reproduce as it slowly travels downstream (Reynolds, 2000). Connection of these dead zones to the main channel will also provide a constant source of algal inoculum to the river. This conclusion is further supported by the data for the River Thames at Hannington Wick, which lies within the "natural" river cluster in Figure 5, despite all the other River Thames sites being within the "rivers with canals" relationship. This is because the Hannington Wick site is upstream of the navigable part of the River Thames, and therefore does not have locks and associated flow impediments. (The River Thames is navigable up to the confluence with the River Coln). The relationship between TP and chlorophyll for the "rivers with canals" subset is very similar to the TP / chlorophyll relationship observed for temperate lakes by Van Nieuwenhuysen et al., (1996).

3.4 Effect of residence time on phytoplankton biomass

The distance from the monitoring site to the river source was used as an approximate indicator of residence time within each river (Table 1). The distances to source were calculated using a GIS application, the Centre for Ecology and Hydrology's Intelligent River Network (Dawson et al., 2002). There was a strong correlation between upstream river length and average chlorophyll concentration (between February 2009 to July 2011) (Figure 6) ($R^2 = 0.82$). Distance to source was also closely correlated with the maximum observed chlorophyll concentration throughout the 30 month monitoring period.

Maximum chlorophyll concentration = $(1.7728 \times \text{Distance to source}) - 10.121$ ($R^2 = 0.70$).

Residence time therefore has a major impact on phytoplankton biomass in the Thames basin. The strong link between chlorophyll concentration and residence time has been made in previous studies of the Thames (Neal et al., 2006) and other rivers (Greenberg, 1964). However, phosphorus concentrations also appeared to have some control on phytoplankton biomass, from observing the increased chlorophyll levels present in some of the more nutrient-enriched tributaries, such as the River Ray and Thame. Previous studies have also shown that other chemical determinands, such as dissolved reactive silicon and nitrate concentration, could also control phytoplankton biomass. Stepwise regression analysis was applied to the complete data set, using Minitab statistical software, release 15, (Minitab Inc., State College, Pennsylvania, USA) which showed that distance to source and SRP concentration produced the strongest model to predict maximum observed chlorophyll concentrations during the monitoring period. Adding the SRP concentration to the distance-to-source regression model increased the R^2 from 0.70 to 0.74, and the adjusted R^2 from 0.69 to 0.71. Adding TP as an alternative second independent variable raised the R^2 by a similar

amount. The addition of other determinands within the data set (average TP, nitrate and dissolved reactive silicon concentrations, average river flow) as a third variable in the distance-to-source / SRP concentration regression model did not improve the prediction of maximum chlorophyll concentration, producing reductions in the adjusted R^2 values. This shows that river length has by far the greatest effect on the size of the phytoplankton bloom in these rivers, with phosphorus concentration also playing a minor role.

To visualize how phosphorus concentrations specifically affect chlorophyll concentrations, rivers of similar length were extracted from the data set. Figure 7 shows chlorophyll time-series data for 2009 for the five monitoring sites that were ca. 30 km (± 2 km) from the river source. The most phosphorus-enriched river, the River Ray (average TP in 2009 = 548 $\mu\text{g l}^{-1}$) had by far the highest maximum and average chlorophyll concentrations (110 and 20.8 $\mu\text{g l}^{-1}$ respectively). The River Ock and Cole (TP concentrations of 316 and 319 respectively) had the next highest average chlorophyll concentrations (5.6 and 10.0 $\mu\text{g l}^{-1}$), with very similar concentrations through the March to June period. The river with the lowest average TP concentration, the River Leach (average TP concentration = 31 $\mu\text{g l}^{-1}$), had the lowest average chlorophyll concentration (2.8 $\mu\text{g l}^{-1}$), and did not appear to have a phytoplankton bloom during the spring and summer period of 2009. The five rivers of ca. 50 km (± 8 km) length also showed a similar strong correlation between maximum chlorophyll concentration and average TP concentration ($R^2 = 0.71$).

3.5 Nutrient limitation of phytoplankton blooms

Previous studies have shown that during the phytoplankton blooms that occurred annually in the River Thames between 1980 and 1996, maximum chlorophyll concentrations at the town of Reading were always ca. 250 to 350 $\mu\text{g l}^{-1}$, and never exceeded 370 $\mu\text{g l}^{-1}$ (Kinniburgh and

Barnett, 2010; Kinniburgh et al., 1997). This present study observed a similar magnitude of blooms in 2009 and 2011. It would seem plausible that chlorophyll concentrations would sometimes attain even higher concentrations, particularly when such a rapid increase in chlorophyll level is observed at the onset of each bloom. The consistency of the maximum chlorophyll concentration values during major blooms imply that phytoplankton biomass in the River Thames is controlled or limited by a factor or resource that restricts the magnitude of the biomass to below $370 \mu\text{g l}^{-1}$ chlorophyll. One possible explanation for these consistent maximum chlorophyll concentrations could be due to self-shading. When the biomass of phytoplankton reaches this concentration, the algae in the lower part of the water column may become light-limited, due to shading by the phytoplankton in the upper water layers (Whitehead and Hornberger, 1984). Another explanation could be silicon limitation of the algae. Previous studies have highlighted the role that dissolved reactive silicon plays in limiting diatom biomass in the Thames (Lack, 1971; Neal et al., 2000b), and depletion of dissolved silicon from the water column is a likely reason that phytoplankton blooms have never exceeded $370 \mu\text{g l}^{-1}$ in the mid and lower River Thames.

3.5.1 River Thames

Reductions in dissolved reactive silicon concentration are observed at almost all study sites within the Thames basin, and coincide with peaks in chlorophyll concentration (Figure 8). This confirms that the annual phytoplankton blooms in March to June, and the secondary blooms in August to September that occur at some of the monitoring sites, have a large diatom component. The algal blooms in the River Thames at Swinford between 2009 and 2011 each resulted in the dissolved reactive silicon concentration reducing from ca. 3.5 mg l^{-1} to ca. 0.5 mg l^{-1} (Figure 8). SRP concentrations also declined, due to bioaccumulation by the phytoplankton, but did not fall below $25 \mu\text{g l}^{-1}$, and nitrate remained above 17 mg l^{-1} .

Therefore, dissolved reactive silicon was becoming scarce, but none of these three macronutrients would be likely to limit phytoplankton growth at these concentrations.

A further 45 km downstream at Wallingford, the dissolved reactive silicon concentrations of the River Thames dropped to as low as 0.1 mg l^{-1} during the major chlorophyll peaks in both the spring of 2009 and 2011, and also the autumn bloom in 2010. In addition, SRP concentrations were reduced to 14 and $23 \text{ } \mu\text{g l}^{-1}$ during the 2009 and 2011 chlorophyll peaks. Therefore, both P and Si were simultaneously in such short supply during these one-week periods that the growth rate of phytoplankton biomass would likely to be silicon limited, and possible phosphorus limited too. However, the SRP concentration only began to become exhausted when the chlorophyll concentrations had already reached $200 \text{ } \mu\text{g l}^{-1}$. A further 32 km downstream of Wallingford at Sonning, SRP concentrations were reduced to below $5 \text{ } \mu\text{g l}^{-1}$ in the River Thames for three and four week periods during the 2009 and 2011 blooms respectively. Dissolved reactive silicon concentration is also reduced, but remains relatively high (minimum concentration of 1.4 mg l^{-1}). This is probably due to the major input of high silicon concentration water from the River Kennet, the largest tributary within this study area, which enters the River Thames ca. 3 km upstream of the Sonning monitoring site (Figure 1). Therefore, phytoplankton growth appears to be phosphorus limited at this site, but again, phosphorus only becomes limiting when the phytoplankton bloom is already well established and chlorophyll concentrations are over $200 \text{ } \mu\text{g l}^{-1}$.

At the downstream extent of the study area (the River Thames at Runnymede) the phosphorus concentration during the 2009 and 2011 phytoplankton blooms was reduced to $<7 \text{ } \mu\text{g l}^{-1}$ for periods of seven and four weeks respectively. During these periods, dissolved reactive silicon concentration was also reduced to below 0.1 mg l^{-1} , and so the phytoplankton biomass

of the Thames was being capped by a lack of both phosphorus and silicon. During the smaller chlorophyll peak of 2010, phosphorus alone was depleted below detectable concentrations. The data from the three phytoplankton blooms suggest that due to the rapid reductions in phosphorus loading in the River Thames since the late 1990s, phosphorus is now becoming the principle limiting factor in capping blooms to ca. $300 \mu\text{g l}^{-1}$ chlorophyll in the lower Thames, rather than silicon. This indicates that if phosphorus concentrations can be lowered further in the River Thames, the periods of phosphorus depletion will increase, and the typical maximum chlorophyll concentrations of ca. $300 \mu\text{g l}^{-1}$ that have been observed in the mid and lower River Thames since 1980 may begin to be reduced due to P limitation.

However, it is important to note that SRP concentration is only reduced to potentially-limiting concentrations in the River Thames due to bioaccumulation by the phytoplankton bloom, and so algal growth-limitation only occurs once the bloom is well established. Reducing the lower River Thames SRP concentration (at the onset of each annual bloom) to a potentially-limiting concentration of ca. $80 \mu\text{g l}^{-1}$ (as identified by Thames phosphorus-limitation experiments by Bowes and co-workers (2012)) may be required to substantially reduce the magnitude of the algal blooms. This would be extremely costly to achieve, as it would require increased levels of P removal at a large number of STWs and possibly major land-use changes. It could be more effective to target phosphorus mitigation in the upper River Thames and upper tributaries, as this would slow the development of the bloom as it moved along the river continuum. Also, because phosphorus loads in the upper Thames are much smaller than the lower Thames, the targeted introduction of P removal at selected STWs in the upper basin could more easily reduce SRP concentrations to algae-limiting concentrations.

3.5.2 River Kennet

Data from the River Kennet in particular implies that phosphorus has begun to restrict the size of the phytoplankton bloom. By applying the linear regression for rivers connected to canals (Figure 5), it can be estimated that the River Kennet would have produced a maximum chlorophyll concentration of ca. $170 \mu\text{g l}^{-1}$ if the average SRP concentration had remained at its 2002 to 2006 levels of ca. $150 \mu\text{g l}^{-1}$, rather than the $45 \mu\text{g l}^{-1}$ maximum chlorophyll concentration observed in this study. Perhaps the strongest evidence for phosphorus limitation of the phytoplankton bloom in the River Kennet is from examining the phosphorus monitoring data (Figure 9), which shows that SRP was reduced to below $10 \mu\text{g l}^{-1}$ for six weeks in the spring and summer of 2010, and seven times during the spring and early summer of 2011 (from ca. $50 \mu\text{g l}^{-1}$ in early spring). These periods of very low SRP concentration coincided with peaks in chlorophyll concentration. Dissolved reactive silicon concentrations dipped sharply (again coinciding with chlorophyll concentration peaks), but remained at relatively high concentrations ($>4.5 \text{ mg l}^{-1}$ silicon). Previous phosphorus limitation studies on the upper River Kennet have shown that SRP concentrations of less than $60 \mu\text{g l}^{-1}$ begin to limit algae, and algal growth rate is reduced by a third when SRP concentrations are reduced to $30 \mu\text{g l}^{-1}$ (Bowes et al., 2010a). Therefore, SRP concentrations of less than $10 \mu\text{g l}^{-1}$ must significantly reduce the ability of phytoplankton to grow and reproduce. This is strong evidence that the phytoplankton bloom in the lower River Kennet at Woolhampton is now being limited by phosphorus concentration.

4 Conclusions

- This study has shown that the average chlorophyll concentrations observed in rivers across the Thames basin are very closely associated with river length, indicating that

water residence time, and not phosphorus concentration, is the key variable in determining phytoplankton biomass.

- Rivers that are connected to canals, or have extensive lock systems, have ca. six times higher maximum chlorophyll concentrations than rivers that do not have such impoundments with the same phosphorus concentration (Figure 5), which further demonstrates the importance of residence time on phytoplankton biomass. Removing impoundments and dead-zones, and stopping water transfers between rivers and canals may be an effective way for catchment managers to reduce phytoplankton blooms and to improve river ecology. These relationships between river length and degree of impoundment with chlorophyll concentration indicate that changing the physical, rather than the chemical conditions of a river could be a more effective means of controlling excessive phytoplankton growth.
- River phosphorus concentration does play a role in determining both maximum and average chlorophyll concentrations. Phosphorus-enriched rivers have larger phytoplankton blooms than nutrient-poor rivers of a similar length.
- Reductions in phosphorus concentration in the River Thames may now be beginning to restrict and cap the size of phytoplankton blooms in the mid and lower River Thames, due to phosphorus limitation, as P is becoming depleted for periods of up to four weeks during the spring and early summer phytoplankton-bloom period. Prior to these water quality improvements, blooms appear to have been capped by the exhaustion of the dissolved reactive silicon supply alone. As further reductions of phosphorus loadings to the River Thames are made, to comply with the European Union's Water Framework Directive, this period of phosphorus exhaustion will increase, and the maximum chlorophyll concentrations (of around $300 \mu\text{g l}^{-1}$) that have been regularly observed since the 1980s may begin to be reduced, due to this

algal phosphorus-limitation / phosphorus-silicon co-limitation during the late spring / early summer period.

- Nitrate concentrations remain high throughout the annual cycle for all monitoring sites, and there was no link between NO_3 concentration and either average or maximum chlorophyll concentrations, indicating that phytoplankton were not nitrogen-limited in any of the rivers in this study. Therefore, mitigation measures that only deliver reduced nitrate concentrations in the Thames basin will have no impact on phytoplankton blooms.
- The River Kennet also has extended periods (up to 7 weeks during the spring to early summer algae growing season) where phosphorus concentrations were very low (below $10 \mu\text{g l}^{-1}$), following a major improvement in water quality since the late 1990s. Despite this river being directly connected at multiple locations to the adjacent Kennet and Avon Canal, and being the longest tributary in the study (both of which will greatly increase the residence time), it has relatively low chlorophyll concentrations. This indicates that the lack of phosphorus through the growing season is now limiting phytoplankton growth, and the reduction in phosphorus loading could be delivering lower algal blooms in the River Kennet.

The River Kennet may provide a template for catchment managers, and shows what is possible when phosphorus concentrations in the rivers of the Thames basin are reduced to potentially-limiting concentrations. However, reducing the pre-bloom SRP concentration of the mid to lower River Thames from $> 200 \mu\text{g l}^{-1}$ to the potentially growth-limiting concentration of $80 \mu\text{g l}^{-1}$ (Bowes et al., 2012) will be extremely costly and potentially difficult to achieve. Other potential mitigation measures, such as increasing the riparian tree

shading in the upper river (which could have the potential to reduce algal growth rate in the River Thames by up to 50% (Bowes et al., 2012)) and reducing residence time by removing impoundments and connections to canals may be needed, alongside phosphorus mitigation, to reduce the magnitude of phytoplankton blooms and to deliver good ecological status in the future.

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Acknowledgements

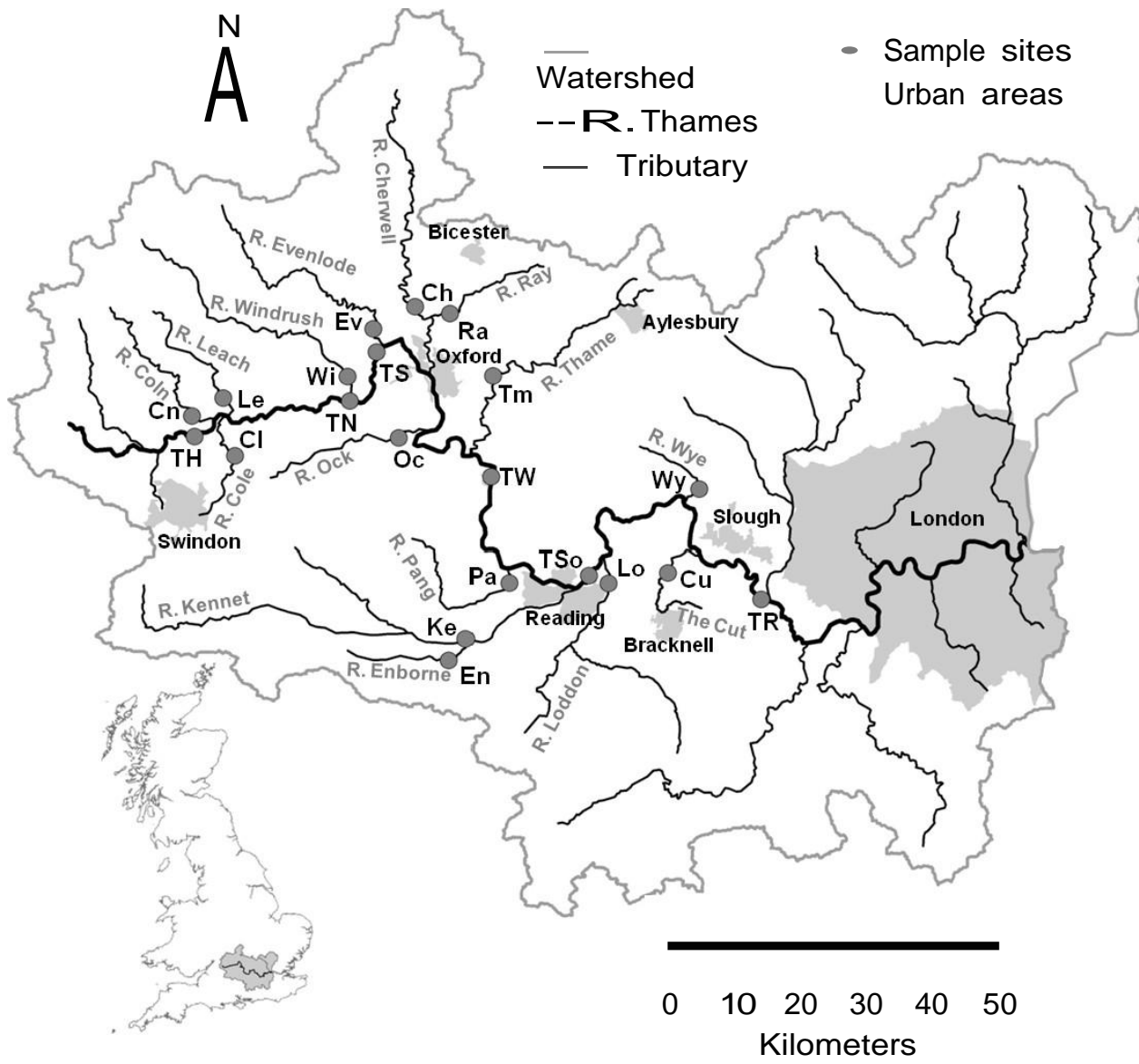
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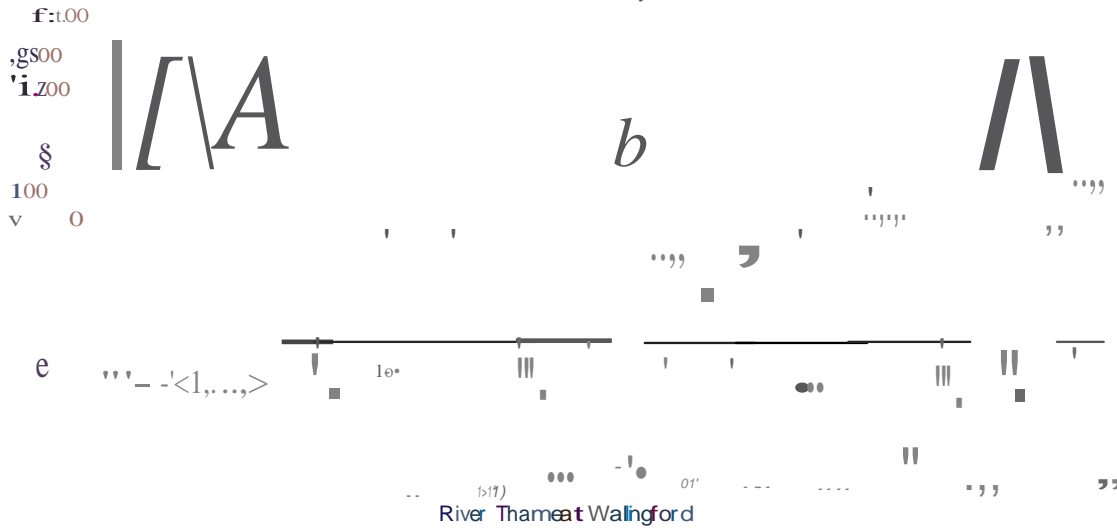
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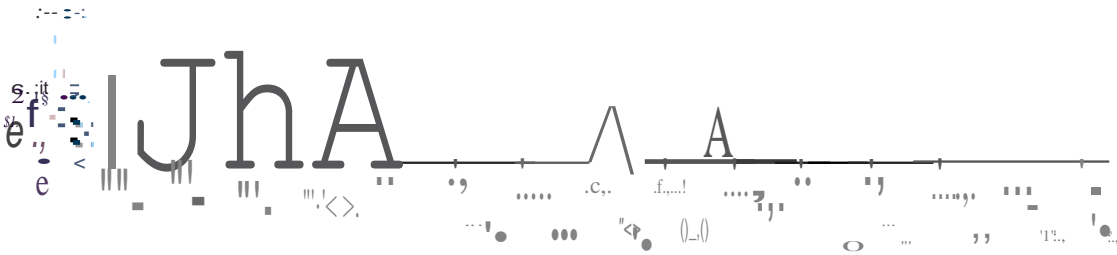
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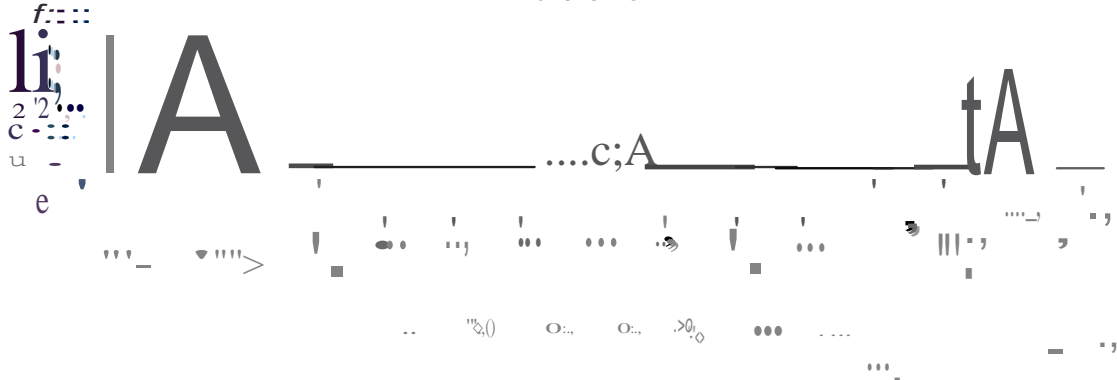
River Thames at Runnymede



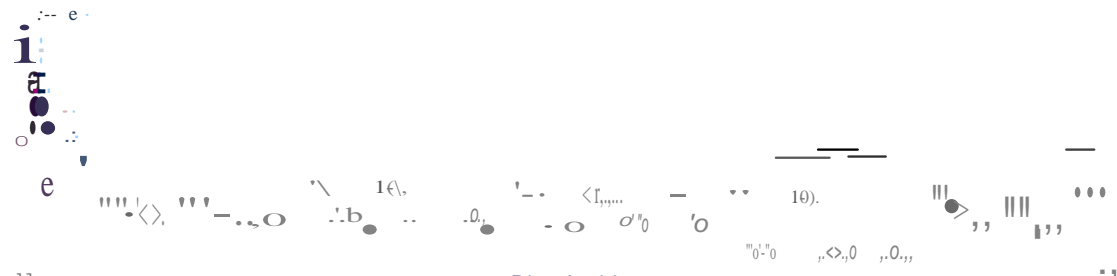
River Thames at Walingford



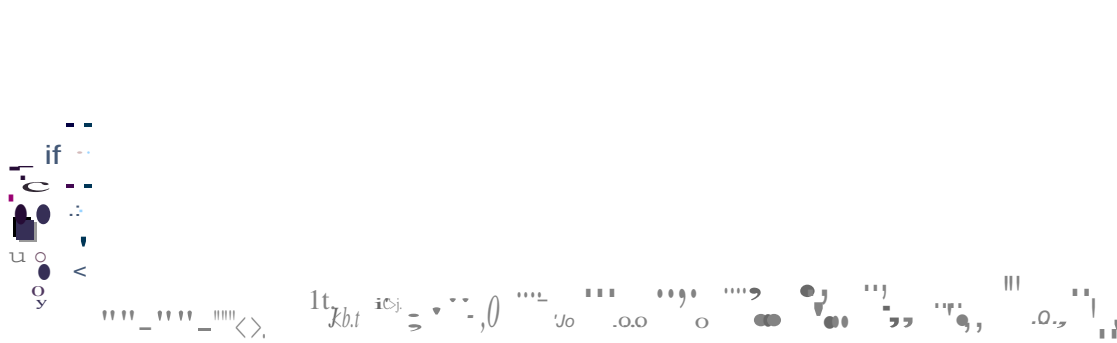
River Cherwell



River Cole



River Lodden






Figure 2

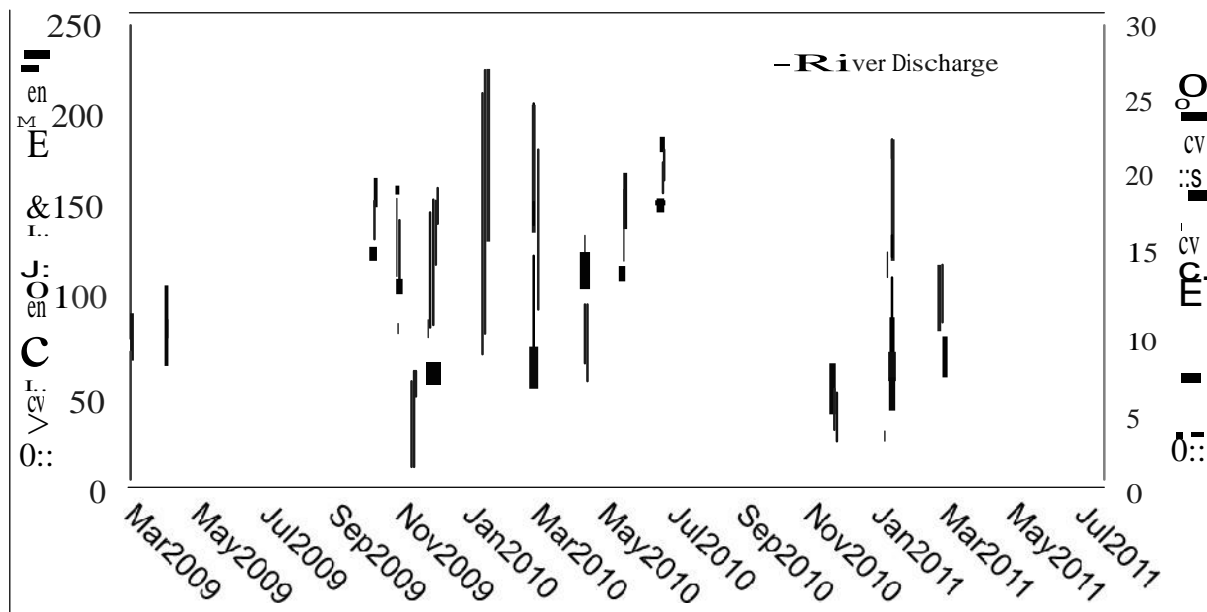


Figure 3

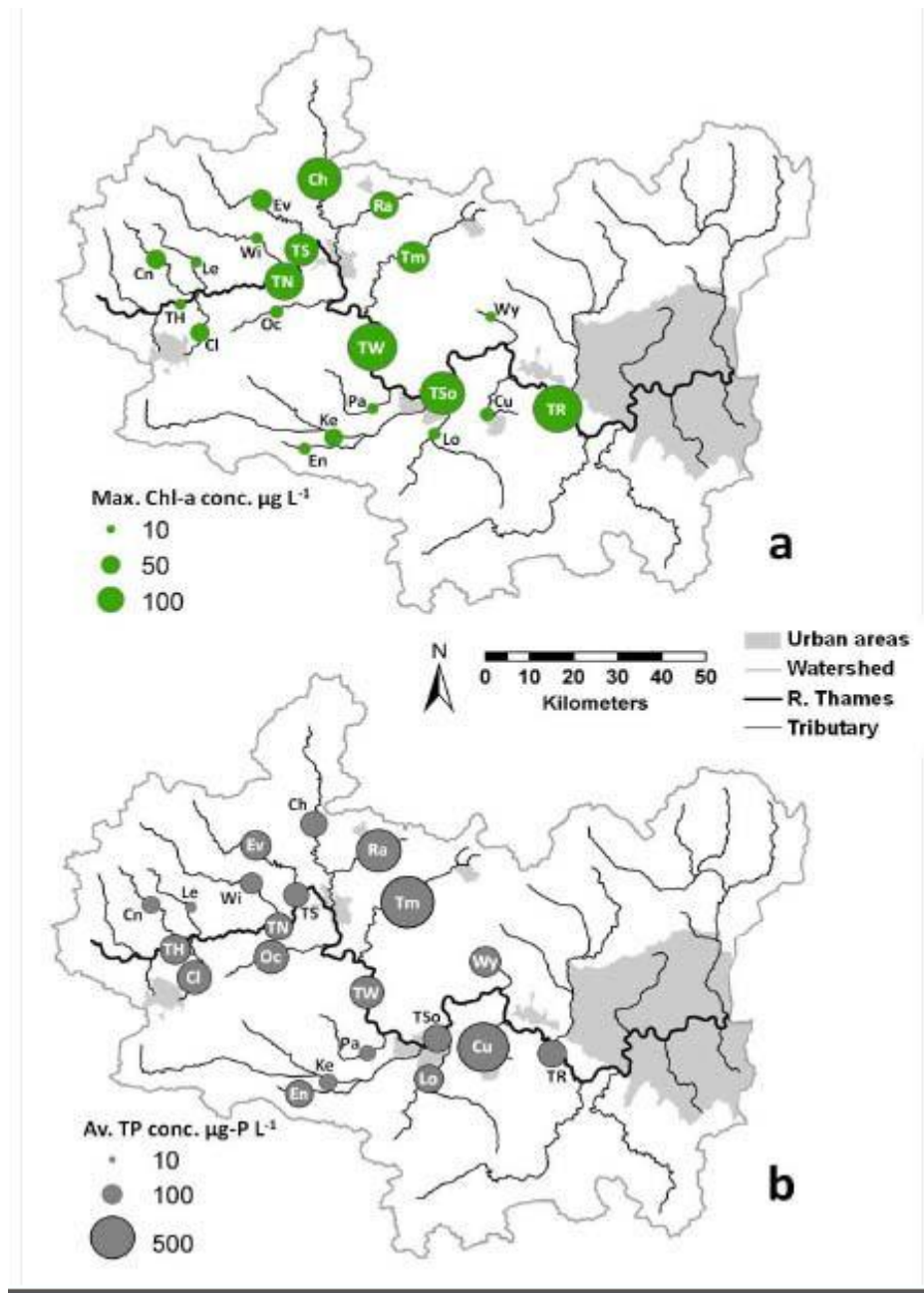


Figure 4

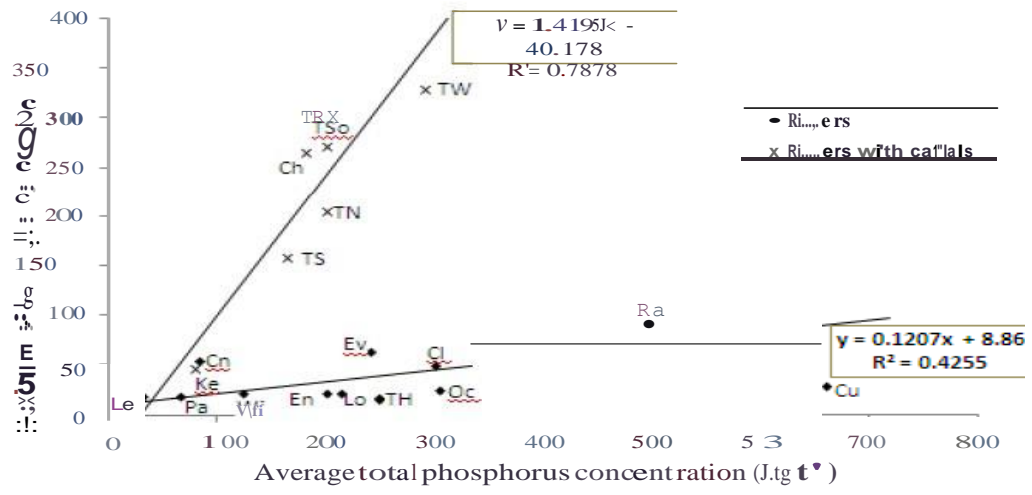


Figure 5

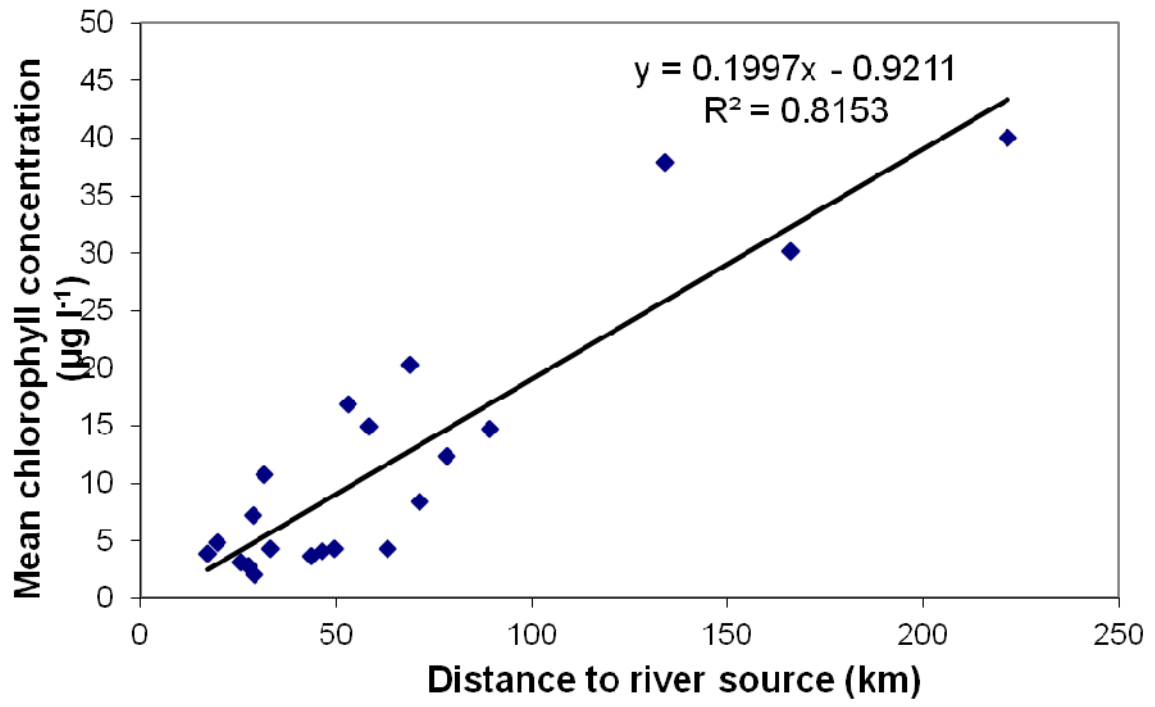


Figure 6

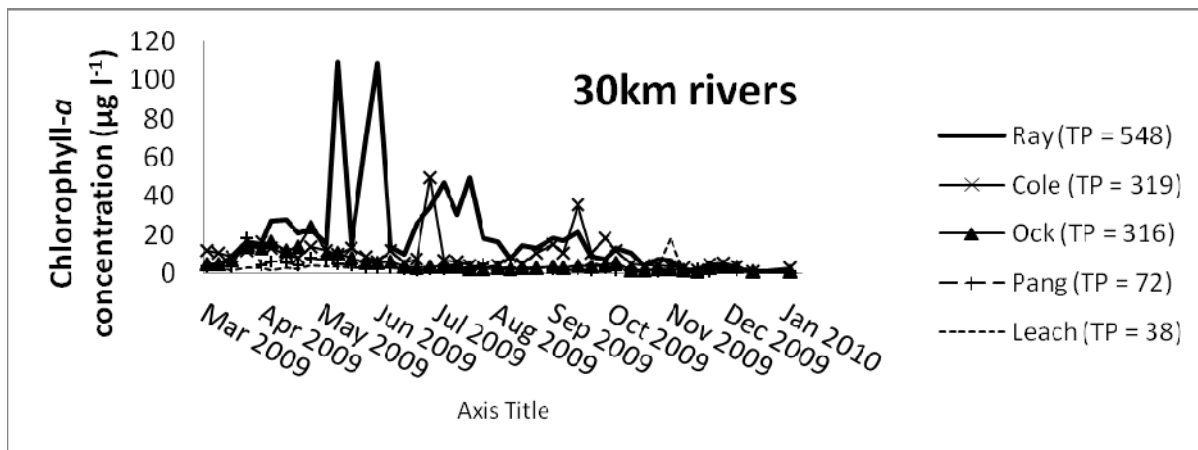


Figure 7

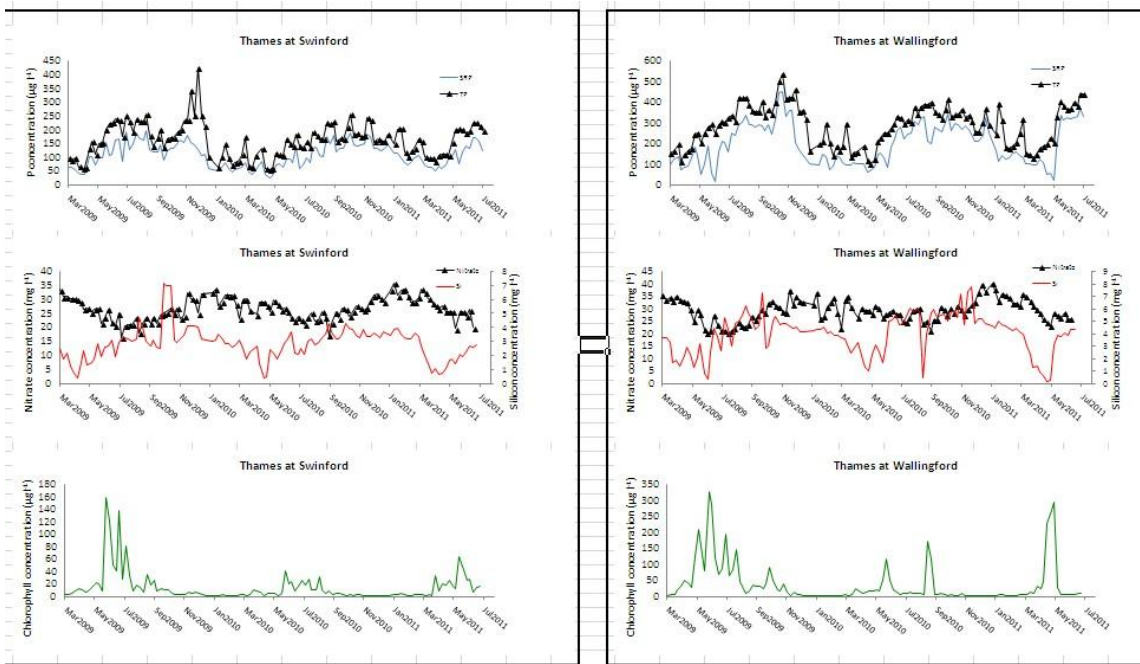


Figure 8a

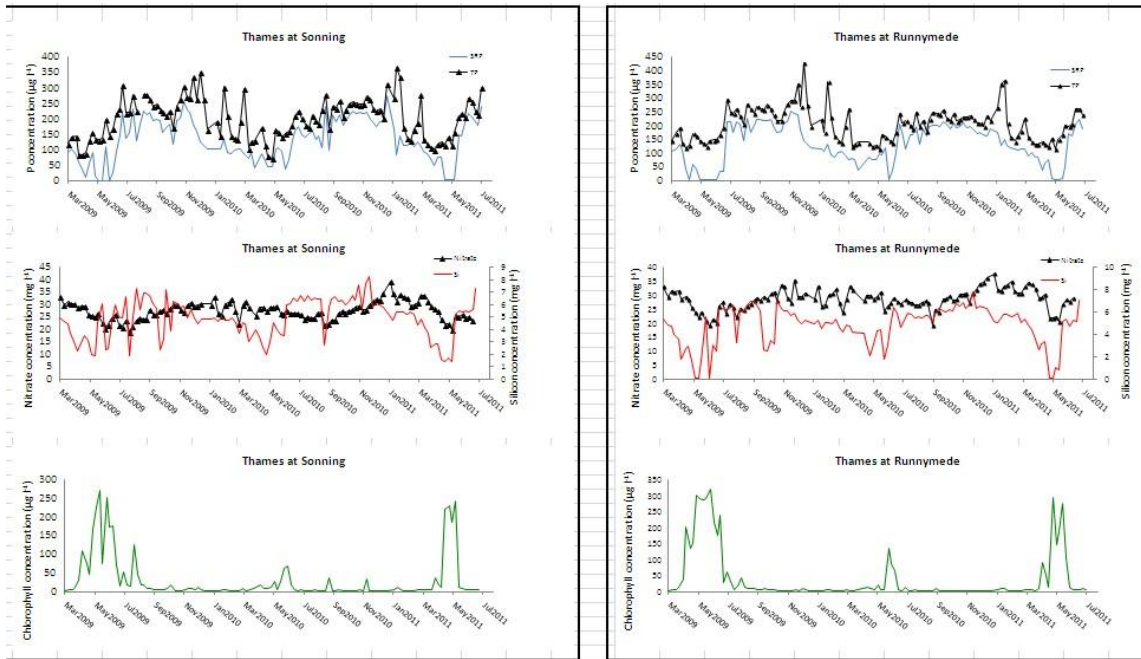


Figure 8b

Table 1

Site code	River	Sampling site	Sampling period	Chlorophyll-a (µg/l)			Soluble reactive phosphorus (µg/l)	Total phosphorus (µg/l)	Dissolved reactive silicon (µg/l)	Nitrate (mg/l)	River discharge (m ³ /s)	Distance to (km)
				Maximum			Mean	Mean	Mean	Mean	Mean	
				2009	2010	2011						
TH	Thames	Hannington Lock	Sept 2009 - July 2011		12	17	175	245	3.4	30.7	4.0	46.5
TN	Thames	Newbridge	Feb 2009 - July 2011	198	77	204	144	199	3.2	26.6	8.3	78.4
TS	Thames	Swinford	Feb 2009 - July 2011	158	40	65	109	163	2.8	26.2	11.2	89.2
TJ	Thames	Wallingford	Feb 2009 - July 2011	328	171	295	201	290	3.9	28.5	30.2	134.0
TSo	Thames	Sonning	Feb 2009 - July 2011	271	69	244	136	200	4.8	27.1	36.6	166.1
TR	Thames	Runnymede	Feb 2009 - July 2011	322	135	295	132	206	4.7	27.5	46.8	221.7
Cn	Coin	Wallingford	Feb 2009 - July 2011	8.6	5.3	42	59	84	2.6	26.5	2.1	43.6
C1	Cole	Lynt Bridge	Feb 2009 - July 2011	49	9.3	43	224	298	6.2	19.5	0.9	28.9
Le	leach	lechlade Mill	Feb 2009 - July 2011	48	3.6	4.7	17	31	2.4	32.4	0.6	29.0
Uj	Windsor	Newbridge	Feb 2009 - July 2011	18	9.6	20	79	124	2.3	29.8	3.0	63.0
EY	Evenlode	Cassington Mill	Feb 2009 - July 2011	63	42	41	162	239	2.6	25.7	3.3	58.4
Ch	Cherwell	Hampton Poyle	Feb 2009 - July 2011	265	64	203	110	181	3.1	26.4	4.4	68.9
Ra	Ray	Islip	Feb 2009 - July 2011	110	44	24	405	487		34.4	1.7	31.7
Tm	Thame	Wheatley	Feb 2009 - July 2011	142	58	47	590	720	6.3	37.0	3.1	53.2
De	Ock	Abingdon	Feb 2009 - July 2011	24		21	246	303	6.8	31.7	1.3	33.3
Pa	Pang	Tidmarsh	Feb 2009 - July 2011	18	4.3	7.3	35	66	6.8	28.8	0.6	27.6
Ke	Kennet	Woolhampton	Nov 2009 - July 2011		45	23	29	77	6.5	23.5	7.3	71.3
En	Enborne	Brimpton	Nov 2009 - July 2011		21	12	129	201	6.6	17.1	1.2	25.5
Lo	loddon	Charvillat	Feb 2009 - July 2011	21	15	15	130	213	5.2	33.9		49.6
Cu	The Cut	Paley Street	Feb 2009 - July 2011	19	13	28	491	662	5.9	86.4		19.5
Uj	Uye	Bourne End	Feb 2009 - July 2011		10	15	184	246	6.4	27.1	1.0	17.3

