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Identifying multiple stressor controls on phytoplankton dynamics in the River Thames (UK) using high-frequency water quality data.

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Abstract

River phytoplankton blooms can pose a serious risk to water quality and the structure and function of aquatic ecosystems. Developing a greater understanding of the physical and chemical controls on the timing, magnitude and duration of blooms is essential for the effective management of phytoplankton development. Five years of weekly water quality monitoring data along the River Thames, southern England were combined with hourly chlorophyll concentration (a proxy for phytoplankton biomass),

flow, temperature and daily sunlight data from the mid-Thames. Weekly chlorophyll data was of insufficient temporal resolution to identify the causes of short term variations in phytoplankton biomass. However, hourly chlorophyll data enabled identification of thresholds in water temperature (between 9 and 19 ^{o}C) and flow (less than 30 m^3 s^{-1}) that explained the development of phytoplankton populations. Analysis showed that periods of high phytoplankton biomass and growth rate only occurred when these flow and temperature conditions were within these thresholds, and coincided with periods of long sunshine duration, indicating multiple stressor controls. Nutrient concentrations appeared to have no impact on the timing or magnitude of phytoplankton bloom development, but severe depletion of dissolved phosphorus and silicon during periods of high phytoplankton biomass may have contributed to some bloom collapses through nutrient limitation. This study indicates that for nutrient enriched rivers such as the Thames, manipulating residence time (through removing impoundments) and light / temperature (by increasing riparian tree shading) may offer more realistic solutions than reducing phosphorus concentrations for controlling excessive phytoplankton biomass.

1 Introduction

River phytoplankton comprise the autotrophic components of the suspended microbial community, and largely consist of diatoms, chlorophytes, dinoflagellates and cyanobacteria. Phytoplankton blooms can pose a serious risk to water quality, and may result in major disruptions to the structure and function of aquatic ecosystems. Excessive algal growth can result in shifts in species composition, including the loss of macrophyte and macroinvertebrate communities, and the low dissolved oxygen concentrations that often accompany the cessation of blooms can lead to fish kills (Carpenter et al., 1998; Hilton et al., 2006). They can cause significant financial loses to the water industry, due to filter blockages at water abstraction points and toxin, taint and odour problems produced by cyanobacterial communities, and can greatly affect the leisure and tourism industry (Dodds et al., 2009; Pretty et al., 2003; Whitehead et al., 2013). It is vital that the controls and causes of riverine phytoplankton blooms are identified and understood, so that effective measures can be adopted to reduce the risk of severe and damaging blooms in the future, particularly because they are predicted to increase in magnitude under future climate change scenarios (Johnson et al., 2009; Whitehead et al., 2013).

Phytoplankton bloom development is relatively well understood in lakes, and well-established conceptual models exist, describing the annual pattern in algal biomass and community succession, principally controlled by the impacts of light, grazing and nutrient availability (Sommer et al., 2012; Sommer et al., 1986). In contrast, there has been relatively little research on river phytoplankton dynamics, and the level of understanding is relatively limited compared to lake systems (Reynolds, 2000). Phytoplankton blooms in rivers have traditionally been attributed to high nutrient concentrations, particularly phosphorus (Chetelat et al., 2006; Herath, 1997; Vollenweider, 1968). However, there are a growing number of riverine studies that suggest that physical factors also play an important role in controlling phytoplankton dynamics. The importance of river flow rate, residence time and the presence of aggregated dead-zones within the river channel have been shown to have a major impact on phytoplankton biomass (Bowes et al., 2012a; Reynolds, 2000). Other studies have highlighted the impact of multiple stressors on phytoplankton dynamics. Flow and light intensity were identified as the key controls on bloom dynamics for agricultural streams in Illinois (Figueroa-Nieves et al., 2006) and the River Elbe, Germany (Hardenbicker et al., 2014). Other abiotic combinations that have been proposed include flow and water temperature (Desortova and Puncochar, 2011), flow, temperature and nutrient concentration (Larroude et al., 2013; van Vliet and Zwolsman, 2008), and flow, temperature and light (Balbi, 2000; Reynolds and Descy, 1996; Waylett et al., 2013). The impacts of invertebrate grazing (Lazar et al., 2012; Waylett et al., 2013; Whitehead et al., 2015), self-shading (Whitehead and Hornberger, 1984) and inhibition due to high light intensities (Whitehead et al., 1997) have also been postulated as a mechanism for limiting phytoplankton biomass and causing bloom cessation in modelling studies of the River Thames catchment, UK. The wide variety of potential stressor combinations that have been suggested by these studies make it very difficult to produce a conceptual model of the processes that control phytoplankton biomass in rivers. Dynamic models of the Thames have tried to represent the above processes, but have found it difficult to produce satisfactory predictive ability, especially during the late summer period when light, temperature, residence time and nutrient concentrations are all typically at their maxima but chlorophyll concentrations are low (Lazar et al., 2012; Waylett et al., 2013)

One potential explanation for this lack of consensus arising from the various scientific approaches could be the lack of suitable and comprehensive observational data that cover all of the potential physical and chemical controls identified in the studies above. The data also need to be taken at an appropriate temporal resolution to capture the potentially rapid changes in flow, temperature, light and nutrient concentrations that typically occur within a dynamic river environment. Perhaps most importantly, the monitoring needs to capture both the rapid changes in phytoplankton biomass during a bloom, and also the annual variations in bloom timing and magnitude over an extended monitoring period.

The development of robust and accurate chlorophyll fluorescence probes now offers an opportunity to produce the high-frequency, long term river chlorophyll concentration data that is needed to elucidate the factors controlling phytoplankton biomass. When deployed at water quality monitoring stations in flow-gauged rivers (particularly alongside other multi-parameter sondes (Wade et al., 2012)), these chlorophyll probes may provide the comprehensive data sets that are key to increasing our understanding of phytoplankton dynamics (Catherine et al., 2012; Gregor and Maršálek, 2004) and provide potential early warnings of bloom development (Ye et al., 2014).

This study aims to identify the controls on the timing, magnitude and duration of phytoplankton blooms in the River Thames, UK, utilising five years of weekly laboratory and hourly chlorophyll probe data. These chlorophyll concentration data will be combined with hourly flow and water temperature, daily sunshine durations and weekly nutrient concentration data, to investigate multiple stressor interactions and to identify physical and chemical thresholds for phytoplankton growth in the River Thames.

1.1 Site description

The River Thames is the second longest river in the United Kingdom, with a total length of 354 km from its source in the Cotswold Hills to its tidal limit at Teddington Lock in south west London and a catchment area of 9948 km^2 (Marsh and Hannaford, 2008). The Thames basin contains the city of London, and other major urban centres, including Swindon, Oxford, Slough and Reading (Figure 1). The basin has a high human population density of approximately 960 people km^{-2} (Merrett, 2007), but despite this, much of the upper Thames basin is relatively rural (Environment Agency, 2009), with

approximately 45 % of land area being classified as arable, 11 % woodland, 34 % grassland, and only 6% classed as urban and semi-urban development (Fuller et al., 2002). The catchment is predominantly underlain by Cretaceous Chalk geology, with Oolitic Limestones in the upper catchment. The River Thames at Reading has a mean annual flow of 38.9 $m^3 s^{-1}$, a base flow index of 0.68 and a mean annual rainfall of 744 mm (Marsh and Hannaford, 2008).

2 Methods

2.1 River monitoring programme

Water samples were taken at weekly intervals from six points along the length of the River Thames (Figure 1) from February 2009 to September 2013, as part of the Centre for Ecology & Hydrology's (CEH) Thames Initiative Research Platform (Bowes et al., 2012a; Bowes et al., 2014). Sub-samples were immediately filtered through a 0.45 µm cellulose nitrate membrane (WCN grade: Whatman, Maidstone, UK) for subsequent soluble reactive phosphorus (SRP), nitrate and dissolved reactive silicon analysis. Unfiltered sub-samples were taken for chlorophyll-a and total phosphorus (TP) analysis. 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* concentrations were used as a proxy for phytoplankton biomass, and were determined by filtering samples through a GF/C grade filter paper (Whatman, Maidstone, UK), overnight pigment extraction using 90 % acetone, and then quantified 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 concentrations were determined on a filtered sample, using the phosphomolybdenum blue colorimetry method (Murphy and Riley, 1962; Neal et al., 2000). Samples were analysed within 24 hours, to minimise errors associated with sample instability (House and Warwick, 1998). Dissolved reactive silicon concentration (termed silicon (Si) throughout the remaining paper) was determined by reaction with acid ammonium molybdate, followed by a reduction step using an acidified tin (II) chloride solution to form intensely coloured molybdenum compounds,

which were quantified spectrophotometrically using a Descrete Analyser (Auto Analyser 2; Seal Analytical, Fareham, UK) (Mullin and Riley, 1955). Nitrate-N concentration was analysed by ion chromatography (Dionex DX500).

High-frequency (hourly) chlorophyll and temperature data for the River Thames at Reading (Site 5; Figure 1) were produced using a YSI 6600 sonde (YSI Inc. Yellow Springs, USA) at the UK Environment Agency's automatic monitoring station at Caversham, Reading (Site 5; Figure 1). The sondes were calibrated every 4 weeks using standard operating procedures.

2.2 Additional data sets

Environment Agency flow data for the River Thames at Reading were supplied by the CEH National River Flow Archive. Daily sunshine hours data were produced using a Campbell-Stokes sunshine recorder, and provided by the Centre for Ecology and Hydrology's meteorological station at Wallingford.

3 Results and Discussion

3.1 Weekly water quality monitoring data

Weekly chlorophyll-a concentration data from six monitoring points along the River Thames between February 2009 and September 2013 are shown in Figure 2. The chlorophyll blooms in each year tend to increase in magnitude along the river continuum, with no substantial peaks observed at the upper site (Hannington Wick; 46.5 km from source) and reaching a maximum chlorophyll concentration in the middle reaches of the River Thames at Wallingford and Sonning (134 km and 166 km from the river source respectively). This increase in chlorophyll concentration with increasing river length has been noted in a previous study of the tributaries of the Thames basin, and attributed to increasing residence time (Bowes et al., 2012a). The levelling out of the chlorophyll concentration in the lower reaches of large European rivers has also been widely reported (Reynolds, 2000), and attributed to light limitation of phytoplankton through self-shading (Whitehead and Hornberger, 1984). The chlorophyll peaks also tend to increase in duration downstream, with the sporadic spikes observed at the upper Thames sites at Newbridge and Swinford, coalescing into broader, more consistent chlorophyll concentrations at the

downstream sites. It is important to note that due to the potentially short duration chlorophyll spikes observed at the upper Thames sites, there would be a significant loss of information by employing a weekly sampling regime. For instance, it is unlikely that these weekly observations will capture the real maximum chlorophyll concentration in these upper Thames sites, and could easily miss entire peaks if their duration is only a few days.

There are clear differences in the magnitude, duration and timing of the chlorophyll blooms in each year. The 2009 growing season produced the largest, most sustained bloom, reaching >320 µg l^{-1} at both Wallingford and Runnymede, and the chlorophyll concentration remained above 50 µg l^{-1} for a period of 11 weeks in the lower Thames at Runnymede (Figure 1; site 7). In contrast, 2010 only produced a maximum chlorophyll concentration of 135 µg l^{-1} at Runnymede, and the peak only lasted 3 weeks. In 2011 and 2012, the chlorophyll peaks were as large as in 2009, but much shorter in duration (5 and 3 weeks respectively). In 2013, a large and sustained chlorophyll bloom was restricted to the lower Thames sites only. The commencement of the chlorophyll blooms each year was relatively more consistent, beginning in the first week in April in 2009, 2011 and 2012, although the 2013 bloom commenced a few weeks later and the 2010 bloom didn't start until the end of May. Therefore, the smallest chlorophyll blooms tended to occur in years when their commencement was delayed (2010 and 2013), but the largest, most sustained bloom of 2009 didn't begin earlier than other years. Previous studies of the River Thames have shown that marked differences in the size, duration and timing of the chlorophyll blooms have been occurring since the 1980s (Kinniburgh and Barnett, 2010; Kinniburgh et al., 1997; Neal et al., 2006; Young et al., 1999).

These marked differences in chlorophyll dynamics over the five year monitoring period were difficult to explain using the weekly water temperature, macronutrient concentration, flow and light data (Table 1; Supplementary figure S1). The two largest blooms occurred in 2009 and 2011, which also had the highest average water temperatures and lowest flows through the February to September growing period, implying that temperature and residence time may be key factors controlling phytoplankton biomass. However, previous studies of the River Thames at Reading have shown that there were very

low chlorophyll concentrations during the 2004-2006 drought period, when water temperatures were also likely to be elevated and flow rates were low (Kinniburgh and Barnett, 2010).

There were no clear linear relationships between the weekly chlorophyll concentration and water temperature, flow, nutrient concentration and daily sunshine hours (Supplementary Figure 1), implying that phytoplankton biomass is either controlled by a complex combination of these multiple stressors and strong memory effects, or by a parameter that is not within this dataset. Flow played an important role, with average chlorophyll concentrations of $\geq$50 µg l^{-1} only occurring at flows below ca. 30 m^3 s^{-1} (Supplementary Figure 1). However, the correlation coefficient was relatively poor (r = 0.25), with most observations at flows below 30 m^3 s^{-1} having chlorophyll concentrations within the typical low range of <20 µg l^{-1}. This suggests that phytoplankton growth is being suppressed by other multiple factors e.g. light-, temperature- or nutrient limitation. The relationship with water temperature was less clear, but indicated that phytoplankton growth was inhibited at temperatures below approximately 10^{o}C. The highest chlorophyll concentrations occurred between 12 and 24 ^{o}C, but again the majority of observations within this temperature range were very low, resulting in a correlation coefficient of only 0.34. Again, this suggests that multiple factors are limiting periphyton growth. The two potentially-limiting macronutrients for phytoplankton within the River Thames system; soluble reactive phosphorus and dissolved reactive silicon (which is required by diatoms to construct frustules) (Bowes et al., 2012b), showed negative relationships due to algal uptake resulting in depletion (Bowes et al., 2011), with the highest chlorophyll concentrations coinciding with the lowest P and Si concentrations. (Nitrogen is greatly in excess throughout the monitoring period, never falling below 14 mg NO_3 l^{-1}, due to excessive historic nitrate contamination of the Chalk aquifer, and has therefore not been considered within this study). It appears that nutrient concentrations are sufficiently in excess to allow dense phytoplankton blooms to develop in the River Thames, and it is the blooms that drive the declining nutrient concentrations, rather than nutrient concentrations controlling phytoplankton biomass. Other recent studies of the Rivers Rhine and Elbe in Germany have come to similar conclusions that nutrient concentrations were not influencing the timing or magnitude of phytoplankton biomass development (Hardenbicker et al., 2014). Total sunshine hours also had poor correlation with chlorophyll

concentration (R = 0.22) (Supplementary Figure 1). These poor relationships between the physical and chemical parameters and chlorophyll concentration explain why it has proved difficult to construct a model to predict algal growth in previous studies (Young et al., 1999).

The weekly resolution of this time series data was not sufficient to gain any further understanding of the controls on chlorophyll bloom commencement, magnitude and cessation. The reasons for this were (1) the true maximum magnitude of chlorophyll peaks is unknown due to the infrequent sampling interval, and many intermittent peaks are missed altogether, particularly in the upper reaches of the Thames. (2) At a weekly sampling interval, it was impossible to determine if the chlorophyll concentration was increasing or decreasing at the time of observation, and therefore it could not be determined if the conditions at the time of sampling were favourable or unfavourable for phytoplankton growth. (3) During periods of rapid increase or decrease in chlorophyll concentration, is was not possible to attribute this to a particular factor (such as an intermittent change in nutrient concentration, flow or temperature) that may have occurred through the preceding week. (5) These difficulties are further compounded due to river phytoplankton dynamics being likely to respond to multiple drivers and past conditions, rather than a single physical or chemical factor at the time of sampling. The potential controlling factors (residence time, flow, nutrient concentration, light, temperature, grazing) are all likely to increase along the continuum of most rivers, and so there will be a high level of co-correlation between them. Therefore, to improve understanding of the controls on phytoplankton bloom dynamics, it is beneficial to monitor both the chlorophyll concentration and the potential drivers at the sub-daily frequency necessary to capture rapid phytoplankton dynamics.

3.2 High frequency data

3.2.1 Sub-daily chlorophyll dynamics

The hourly chlorophyll concentration data from the Environment Agency automatic monitoring station at Reading (Figure 1; site 5) demonstrated the rapid, sub-daily phytoplankton dynamics that were operating within this middle section of the River Thames. The onset of blooms were often rapid (Figure 3), with the spring bloom of 2012 beginning on 20th March, and immediately entering an exponential growth phase, producing a doubling of chlorophyll concentration each day until 25th

March. The chlorophyll growth rate began to slow over the next week, and the chlorophyll concentration began to decline on the 3rd April. There was a clear diurnal cycling of the chlorophyll signal during periods of high phytoplankton biomass, with maximum concentrations occurring in mid-afternoon (14:00 to 16:00h) and daily minima occurring in the early hours of the morning (usually 06:00h) (Figure 3). This hourly chlorophyll data provides the potential to develop much greater understanding of the controls on phytoplankton biomass that would not be possible using weekly monitoring data (or certainly not the monthly chlorophyll monitoring that is routinely gathered across the UK). It identifies the specific days that blooms begin to develop or crash, and the observed diurnal cycles could potentially be used in future scientific investigations to infer net phytoplankton growth and death / grazing rates, productivity and phenology under specific physical and chemical conditions.

3.2.2 Single stressor relationships

Hourly chlorophyll concentration data from the automatic water quality monitoring station at Reading were paired to the hourly water temperature data and river flow data at the same site, and to daily sunshine duration. The hourly chlorophyll data were also matched to the weekly SRP and dissolved reactive silicon data observed for the River Thames at Wallingford (approximately 12 km upstream of Reading) in the previous week. Boxplots of this combined data set were used to infer thresholds required for phytoplankton growth / high chlorophyll concentrations (Figure 4). All chlorophyll concentrations >30 µg l^{-1} occurred when river water temperatures were between 9 and 21 ^{o}C, with the vast majority of the high chlorophyll concentrations occurring between 9 and 19 ^{o}C. High chlorophyll concentrations predominantly occurred at flows less than 30 m^3 s^{-1}, which probably relates to longer residence times within the river. At higher flows, residence time will be reduced, and the phytoplankton do not have the required time to reproduce enough generations to produce significant biomass (Reynolds, 2000). These data provide evidence for the temperature and flow thresholds required for increases in chlorophyll concentration. However the majority of the chlorophyll concentrations within these favourable temperature and flow thresholds were extremely low, and there was little change in the median chlorophyll concentrations across the full range of temperatures and flows (<4 µg

chlorophyll l^{-1}) (Figure 4). This suggests that a combination of favourable physical and chemical conditions is required to stimulate the rapid phytoplankton growth that produces high chlorophyll concentrations.

Elevated SRP concentrations did not produce high chlorophyll concentrations (Figure 4). In fact, when the weekly SRP concentrations were above 300 µg l^{-1}, the chlorophyll concentration never exceeded 50 µg l^{-1}. The highest mean chlorophyll concentrations were observed at SRP concentrations of <60 µg l^{-1}, again suggesting (as seen with the weekly data set) that phytoplankton blooms are controlling SRP concentration through uptake, rather than elevated SRP concentrations initiating phytoplankton blooms. When the SRP concentrations were less than 60 µg l^{-1}, chlorophyll concentrations never fell below 45 µg l^{-1}, indicating that phosphorus limitation of phytoplankton does not occur in the middle reaches of the River Thames, due to the high initial P loading to the river. Dissolved reactive silicon showed a similar pattern of low chlorophyll at high Si concentrations and severe Si depletion during phytoplankton blooms (not presented for brevity, but similar to the weekly data relationship in Supplementary Figure 1), thus indicating that diatoms must be a major component of the phytoplankton biomass.

There was a positive relationship between sunshine duration and chlorophyll concentration, with the majority of chlorophyll observations (>30 µg l^{-1}) occurring when there had been over 20 h of sunshine over the previous five days. There was not a marked threshold in the sunshine data, with chlorophyll concentrations greater than 50 µg l^{-1} being observed at all sunshine duration categories. Again, the median chlorophyll concentrations across all sunshine duration categories were very low, ranging from 2.1 to 5.6 µg chlorophyll l^{-1}. So even during periods of extremely sunny weather (>30 h over the preceding five days) there was usually low phytoplankton biomass in the River Thames. This again suggests that other multiple physical or chemical conditions are required alongside long daily sunshine durations before phytoplankton growth can occur.

The lack of a clear sunshine duration threshold is not surprising, as light is a more complex parameter to adequately capture than flow and water temperature, and it can rapidly change on a sub-hourly

timescale. Within this study, a simple measure of daily sunshine duration is used. However, it is likely that phytoplankton response to sunshine will also be affected by its timing (i.e. when these periods of sunshine occur through the day) and periodicity (i.e. whether they occur in one block, or are dispersed through the day). The impact of sunshine hours will also change through the seasons, due to changes in river shading caused by deciduous trees becoming foliated / defoliated each year. Another important light parameter that was not captured within this study was sunlight intensity / photosynthetically active radiation, which is also likely to play a major role in phytoplankton dynamics.

3.2.3 Multiple stressor relationships

Two different indicators were used to investigate the optimal conditions required for phytoplankton growth. Firstly the daily chlorophyll concentration (measured at midday each day) was used (Figure 5a-c) as this was probably the best proxy for total phytoplankton biomass. However, if phytoplankton growth rates suddenly decreased or stopped due to unfavourable physical or chemical conditions, the chlorophyll concentrations are likely to remain high for the following few days, as phytoplankton biomass from the upper catchment is transported downstream to the monitoring point. To deal with this potential bias in the data, a second indicator (the difference between the chlorophyll concentration at 16:00h (usually the peak of the typical diurnal cycle; Figure 3)) and 16:00h the preceding day) (Figure 5d-f) was used as a proxy for phytoplankton daily growth rate.

The 3-dimentional contour plots in Figure 5 show how these two daily phytoplankton growth indicators are impacted by the combined effects of daily sunshine duration, water temperature and flow conditions. Chlorophyll relationships with weekly nutrient data were omitted from this stage, as the data in Figure 4 had demonstrated that they were probably in excess and unlikely to be playing a significant role in controlling the timing or magnitude of blooms in the River Thames.

Both algal indicators (chlorophyll concentration and change in chlorophyll concentration) showed that highest mean biomass and growth rates occurred when both the water temperature was between approximately 12 and 16^{o}C, and flows were below 30 $m^3 s^{-1}$ (Figures 5a and 5d). Figure 5c suggests a

temperature threshold at approximately 9 - 10 ^{o}C, with very low chlorophyll concentrations and daily growth rates below this temperature. There is also an upper temperature threshold of approximately 20 ^{o}C for chlorophyll concentration (Figure 5c). The single isolated area of high chlorophyll growth rate at flows between 120 and 150 $m^3 s^{-1}$ (Figure 5d) is probably related to scouring of benthic algae during storm events. The highest phytoplankton growth rates tended to occur on days with high daily sunshine durations of 11 to 12h (Figures 5b, c, f), but significant chlorophyll concentrations and growth rates could also occur when sunshine hours were as low as 3 h per day (Figures 5c, e, f).

3.3 High-frequency time series analysis

The multi-parameter contour plots in Figure 5 suggest that conditions for all these parameters need to be within certain suitable ranges to enable algal growth and high biomass to develop. The physical thresholds in temperature (9 – 19 ^{o}C) and flow (< 30 $m^3 s^{-1}$) identified from Figure 4, along with the daily sunshine duration of at least 3 h duration per day (estimated from Figure 5) and weekly P and Si concentration data, were applied to the hourly chlorophyll time series data for each individual year from 2009 to 2013. These derived thresholds were then used to test whether they were able to explain the complex hourly chlorophyll dynamics observed in the River Thames at Reading (Figure 6).

3.3.1 2009

This year produced the largest, most sustained bloom of the five year monitoring period (Figure 2). There were five relatively distinct bloom periods. The first began on March 28th, commencing at the first time that the flow fell below the 30 $m^3 s^{-1}$ threshold (Figure 6(a)). There had been a sustained and continuous sunny period since the 14th March, and the water temperature was within the required 9 – 19 ^{o}C range since the 15th March, but the chlorophyll concentration only began to increase when light, temperature and flow were all within the required ranges. This first bloom ended on the 10th April due to three days with low sunshine duration. The second, more sustained bloom began on the 20th April, triggered by a period of sustained sunshine, ending on the 13th May, corresponding with a few days of low sunshine and an increase in flow. Growth rate slowed down from the end of April, due to dull days interspersed between longer sunny periods, but three days with daily sunshine durations below 2 h and

some associated rainfall and increased river flow caused the bloom to rapidly terminate. A period of sustained sunshine from the 16th to 27th May, combined with low flows and water temperature ranging from 14 to 18 ^{o}C caused a rapid increase in chlorophyll concentration. The end of this third bloom corresponded to a day with zero hours of sunshine, water temperatures increasing above the 19 ^{o}C threshold, and the SRP and dissolved Si concentrations reaching potentially limiting concentrations (14 µg P l^{-1} and 0.3 mg Si l^{-1} respectively), and it is therefore unclear which of these individual (or combination of) parameters caused the chlorophyll concentration to decrease. The start of the fourth small chlorophyll peak in late June again corresponded to a period of sustained sunny weather through to mid-July, but this peak soon ended due to the river temperature again exceeding the 19 ^{o}C threshold. The fifth and final peak began on 15th July, when the water temperature fell back below 19 ^{o}C, but this peak was inhibited and finally ended by lack of sustained sunshine.

3.3.2 2010

The first small chlorophyll peak of the year began on 24th April, corresponding with the river flow falling below the 30 m^3 s^{-1} threshold (Figure 6(b)). For the previous three weeks, there had been long durations of sunshine and for much of that time, river temperatures were within the optimal range, but there was no bloom, demonstrating again that light, temperature and flow conditions all need to be within the required thresholds before algal growth can occur. This chlorophyll peak ended due to a period of dull weather and rainfall, resulting in the flow increasing back above the 30 m^3 s^{-1} threshold. The larger second peak in mid-May was triggered by two weeks of relatively sunny weather, but this peak was inhibited by high water temperatures (reaching 21 ^{o}C), followed by a period of dull weather.

There was a third small chlorophyll peak in late August, preceded by a rapid depletion in dissolved silicon concentration (indicating benthic diatom growth) occurring when the water temperature fell below the 19 ^{o}C threshold. This peak was abruptly ended by a rainfall event tripling the river flow. Some of the chlorophyll may be derived from resuspended material due to scouring of benthic biofilms across the catchment. There was very little phytoplankton production in 2010, compared with the other studied years. The main reasons for this were that flows were generally too high for much of the early

growing season, and by the time the flows had fallen below the 30 $m^3 s^{-1}$ threshold, water temperatures were too high to sustain chlorophyll production from the start of June to mid-August.

3.3.3 2011

Dissolved silicon concentrations began to decline in mid-March 2011 (Figure 6c). This corresponded to the point where water temperature increased above 9 ^oC and simultaneously, flow decreased below the 30 $m^3 s^{-1}$ threshold. Benthic diatom growth was therefore occurring in this period, but daily sunshine duration was not high or sustained enough to translate this into significant phytoplankton production (Figure 6(c), peak1). The main chlorophyll peak of 2011 (Figure 6(c), peak 2) commenced on the 13th April, and increased rapidly through a week of bright sunny weather (between 5 and 11 hours sunshine per day). The peak began to decline on the 22nd April, despite the temperature and flow continuing to provide the required conditions for algal growth. The silicon concentration data was only 0.12 mg l^{-1} on the 26th April, which might indicate that this bloom was inhibited by silicon limitation of the diatom community. This highlights why high frequency sub-daily nutrient monitoring (rather than the weekly data presented in this study) is required to fully investigate the potential role of nutrient limitation in controlling phytoplankton dynamics. The chlorophyll concentration began to increase again on the 30th April (Peak 3), during a period of sunny weather, but a few days of dull wet weather, an increase in flow (with its associated decrease in residence time) and continued low silicon and phosphorus concentrations rapidly reduced the chlorophyll concentrations back to background levels.

From mid-May to mid-June, there were periods of very sunny weather (9 to 13 h d^{-1} sunshine duration) and water temperature and flow were well within the required thresholds, but there were no chlorophyll peaks. This period was the only time within the five year monitoring period that could not be explained using the chlorophyll thresholds developed within this study, and suggests that there is a missing stressor or threshold that this present study is not taking into account. This missing stressor could be grazing pressure. The lack of a chlorophyll peak at this time may be due to diatom predation through viral lysis or zooplankton grazing (Waylett et al., 2013). The lack of chlorophyll peaks could also be due to the annual microbial succession, with the diatoms being outcompeted and replaced by another phytoplankton group. Flow cytometry monitoring of the River Thames at Wallingford through this

period showed that the rapid decrease in diatom abundance corresponded to a rapid proliferation of nano- and picochlorophytes (which are not picked up by either the fluorescent chlorophyll probe technique or traditional solvent-based chlorophyll analysis) (Read et al., 2014). A third potential explanation for the lack of chlorophyll peaks through this mid-May to June 2011 period may be that there is a lower flow threshold, below which diatoms cannot maintain their position in the water column and therefore settle out (Balbi, 2000). This explanation is supported by the data in Figure 4(b), which shows that chlorophyll blooms do not usually occur below 10 $m^3 s^{-1}$. (The flow during this mid-May to mid-June 2011 period was within the range 6 and 8 $m^3 s^{-1}$).

There was a final small and short term (6 day) chlorophyll peak in late July 2011. Two weeks prior to this, there was a rapid dip in silicon concentrations to non-detectable levels, and SRP was reduced from 334 µg l^{-1} to 94 µg l^{-1}, coinciding with the period when the water temperature dipped below the 19 ^oC upper threshold, indicating a rapid growth of benthic diatoms in the upper catchment. The resulting short duration peak could be due to sloughing of this biofilm as the river temperature rapidly increased back above the threshold to the annual maximum of 22 ^oC.

3.3.4 2012

The 2012 chlorophyll bloom consisted of a single sustained peak, commencing rapidly in mid-March, corresponding to the first sustained period of uninterrupted sunshine, and the period where the water temperature first increased above the 9 ^oC threshold (Figure 6(d), Peak 1). The maximum chlorophyll concentration (150 µg l^{-1}) was reached at the start of April, when the bloom was abruptly ended due to a period of dull weather. A small peak started to develop after a few days of sunny conditions (Figure 6(d), Peak 2), but chlorophyll concentrations rapidly returned to background levels due to dull wet weather and a resultant small increase in flow. The remainder of the year was untypical, as there were no more chlorophyll peaks from May onwards. This was due to the wet weather resulting in river flows being above the 30 $m^3 s^{-1}$ threshold throughout the majority of the summer. By the end of May, the flow fell to below 30 $m^3 s^{-1}$ and there was sustained sunshine, but by this time, the water temperature was too high to support diatom growth.

3.3.5 2013

The 2013 chlorophyll bloom commenced on 28th April, again corresponding to the time when the flow dropped below the 30 $m^3 s^{-1}$ threshold (Figure 6(e), Peak 1). The bloom declined through early to mid-May, caused by a period of dull weather and flow increase above the 30 $m^3 s^{-1}$ threshold, but could also be potentially due to phosphorus and silicon limitation. A second and third peak corresponded to periods of 10 h sunshine, which were ended by dull weather and too high a water temperature respectively. A final small chlorophyll peak at the end of June was also ended by temperatures again rising above the 19 ^oC threshold and low sunshine durations. There was an extended period of almost continuous sunny weather and low flows (<10 $m^3 s^{-1}$) throughout July, but chlorophyll concentrations remained at background levels due to water temperatures exceeding the 19^oC threshold.

3.3.6 Time series summary

This time series analysis demonstrates that the thresholds identified in Figures 4 and 5 can explain most of the chlorophyll dynamics observed over the five year monitoring period. Blooms only occurred within the 9 to 19 ^oC temperature range and at flows less than 30 $m^3 s^{-1}$. The main driver was sunshine duration, with three or more consecutive sunny days required before chlorophyll concentrations began to increase. The most common cause of bloom cessation was a short succession of dull days with low sunshine hours. These periods sometimes coincided with periods of rainfall, which will also reduce phytoplankton residence time as river flows increase. Therefore, light is a key limiting factor. Exceeding the upper temperature threshold of 19 ^oC appeared to immediately terminate the chlorophyll peaks. This is a key observation, and may provide the basis for much improved phytoplankton models, as it provides a mechanism that explains the low chlorophyll concentrations that are observed during the mid to late summer periods. There are a number of plausible explanations for this upper temperature threshold. It may indicate that the phytoplankton species contributing to the chlorophyll peak (principally diatoms and large chlorophytes) are not well adapted to high temperatures and they could trigger sedimentation as resting stages (e.g. diatom auxospore production) when river water exceeded this temperature. Alternatively, other phytoplankton groups such as nano- and pico-chlorophytes may outcompete them. This temperature threshold may also trigger increased grazing by zooplankton or parasitism by bacteria / viral lysis. There was only one period (mid-May to mid-June 2011) when the

physical conditions were all favourable for an extended period, but there were no chlorophyll peaks or reductions in dissolved silicon concentrations (indicating increasing diatom biomass). Again, this lack of response could be due to phytoplankton succession through the annual cycle, increased grazing rates, or due to the flow being too low to keep the phytoplankton entrained within the water column. The late summer chlorophyll peaks that occurred in 2010 and 2011 were also not fully explained by the thresholds derived from Figure 4. These periods of favourable conditions corresponded with silicon depletions (Figure 6), showing again that when temperature, flow and light conditions are suitable, diatom growth rate increases rapidly, but this growth was confined to periphyton rather than phytoplankton. However, the short-duration chlorophyll peaks actually correspond to small flood events following these periods of silicon depletion, indicating that the cause was biofilm scouring, rather than production within the water column.

Increased nutrient concentrations played no part in initiating any of the blooms. The timing of all the chlorophyll peaks could be explained almost entirely by the physical parameters of water temperature, sunlight duration and flow. However, nutrient limitation could potentially play a part in terminating the major blooms in 2009, 2011 and 2013. Dissolved silicon concentrations were low (0.30, 0.12 and 0.75 mg Si l^{-1} respectively) at the time of each bloom cessation, which could be potentially limiting for diatoms (Lund, 1950) and SRP was depleted to 14 and 37 µg l^{-1} in 2009 and 2013 respectively.

4 Conclusions

This study has highlighted that to gain understanding of the factors controlling algal bloom dynamics, physical, chemical and biological monitoring data need to be acquired at high-frequency timescales that are commensurate with the rapid phytoplankton dynamics that typically occur in rivers. These high-frequency data are becoming easier to acquire with the development of more robust and accurate sondes, nutrient auto-analysers and accompanying telemetry systems (Wade et al., 2012).

This paper presents a simple method of extracting physical and chemical thresholds from high-frequency river monitoring data that offers a simple methodology for predicting the timing of the onset

and cessation of algal blooms. This could provide valuable information and an early warning system for water companies and catchment managers.

The timing and magnitude of chlorophyll peaks in the River Thames can be explained by physical factors alone. River flow, water temperature and sunshine duration over the preceding days were the key controls. Increases in nutrient concentrations did not trigger phytoplankton blooms in the River Thames. Nutrient concentrations had a possible role in the cessation of some major blooms, with dissolved silicon in particular being depleted to possibly limiting concentrations, but most bloom collapses were in response to high temperatures, flow increases and low sunshine hours. However, these observations are based on weekly nutrient observations, and sub-daily dissolved P, N and Si monitoring data would be required to combine with the high-frequency chlorophyll and physical data, to determine the true role of nutrient limitation of phytoplankton blooms.

The lack of chlorophyll blooms in the July and August period of most years appears to be closely linked to high water temperatures, but the reasons for this are unclear. Possible explanations include:

(1) direct temperature inhibition of the chlorophyll-containing phytoplankton groups,
(2) stimulation of the nano- and picochlorophytes population that are thought to outcompete the larger chlorophytes and diatoms in the Thames in mid to late summer (Read et al., 2014),
(3) the high water temperatures stimulating filter feeders and zooplankton grazing, or
(4) increasing viral lysis rates.

It is recommended that additional high-frequency biological monitoring data of the phytoplankton, bacterioplankton and algal-grazing communities are collected to inform tests of these hypotheses. This should be done in conjunction with the inclusion in dynamic river quality models of (i) a partitioning of phytoplankton into constituent groups with specific environmental requirements making up the chlorophyll load (ii) a refined representation of zooplankton grazing. Model applications would also be useful in that they consider the intensity as well as the duration of sunshine. From these, a quantification of the influence of grazing on phytoplankton populations may be achievable.

The findings of this study have important implications for the effective management of the River Thames and similar nutrient-enriched rivers, as it suggests that controlling excessive phytoplankton growth could be more effectively addressed by targeting physical conditions in the river, such as reducing residence times (by removing impoundments and connections to canals) and by managing water temperature and light through providing riparian shading, rather than reducing nutrient loadings. Other studies of the River Thames have come to similar conclusions (Bowes et al., 2012b; Hutchins et al., 2010). It also has implications for the potential impact of future climate change. Warmer drier summers are predicted for southern England, and the lower flows and higher water temperatures may mean that chlorophyll blooms will be larger and longer in duration in the future, and will tend to occur earlier in the year. This could have important implications for river ecosystem biodiversity and functioning.

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List of tables and figures

Supplementary Figures

Table 1. Average physical, chemical and chlorophyll data during the period of potential phytoplankton growth (February to September) for the River Thames at Wallingford.

Year	Water temperature at time of sampling (°C)	River flow ($m^3 s^{-1}$)	Daily sunshine duration (hours)	Total P ($\mu g l^{-1}$)	Nitrate ($mg NO_3 l^{-1}$)	Average chlorophyll-a concentration ($\mu g l^{-1}$)	Maximum chlorophyll-a concentration ($\mu g l^{-1}$)
2009	15.3	23.2	4.3	317	28.3	63	329
2010	12.1	33.1	4.2	277	29.4	16	171
2011	13.1	20.5	4.2	383	29.1	30	295
2012	12.0	44.3	4.2	248	26.5	12	122
2013	12.2	45.4	4.6	275	28.2	16	115

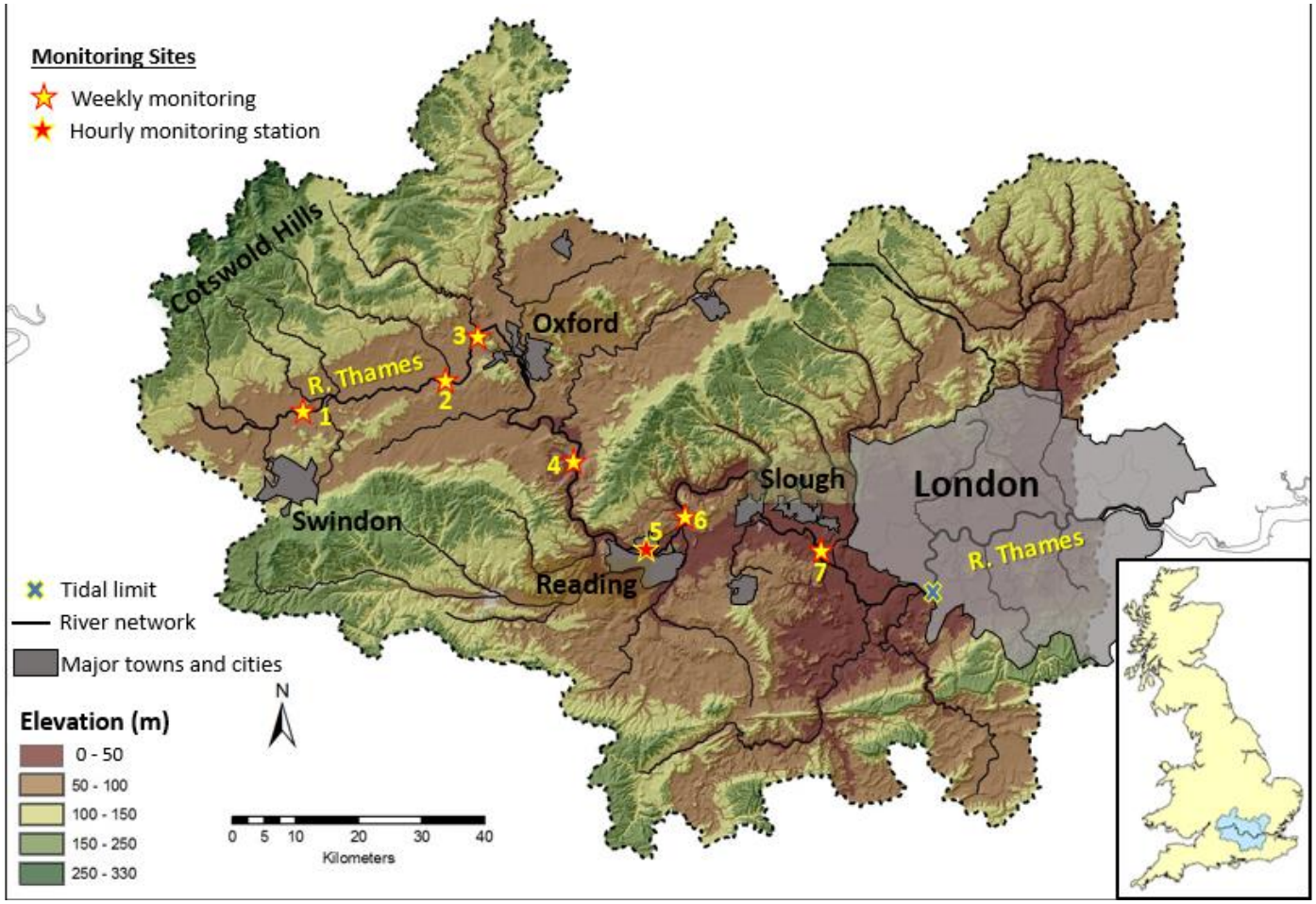


Figure 1. Map of River Thames basin, showing location of River Thames monitoring sites. Site 1 = Hannington Wick; Site 2 = Newbridge; Site 3 = Swinford; Site 4 = Wallingford; Site 5 = Reading (Environment Agency high-frequency monitoring station; Site 6 = Sonning; Site 7 = Runnymede.

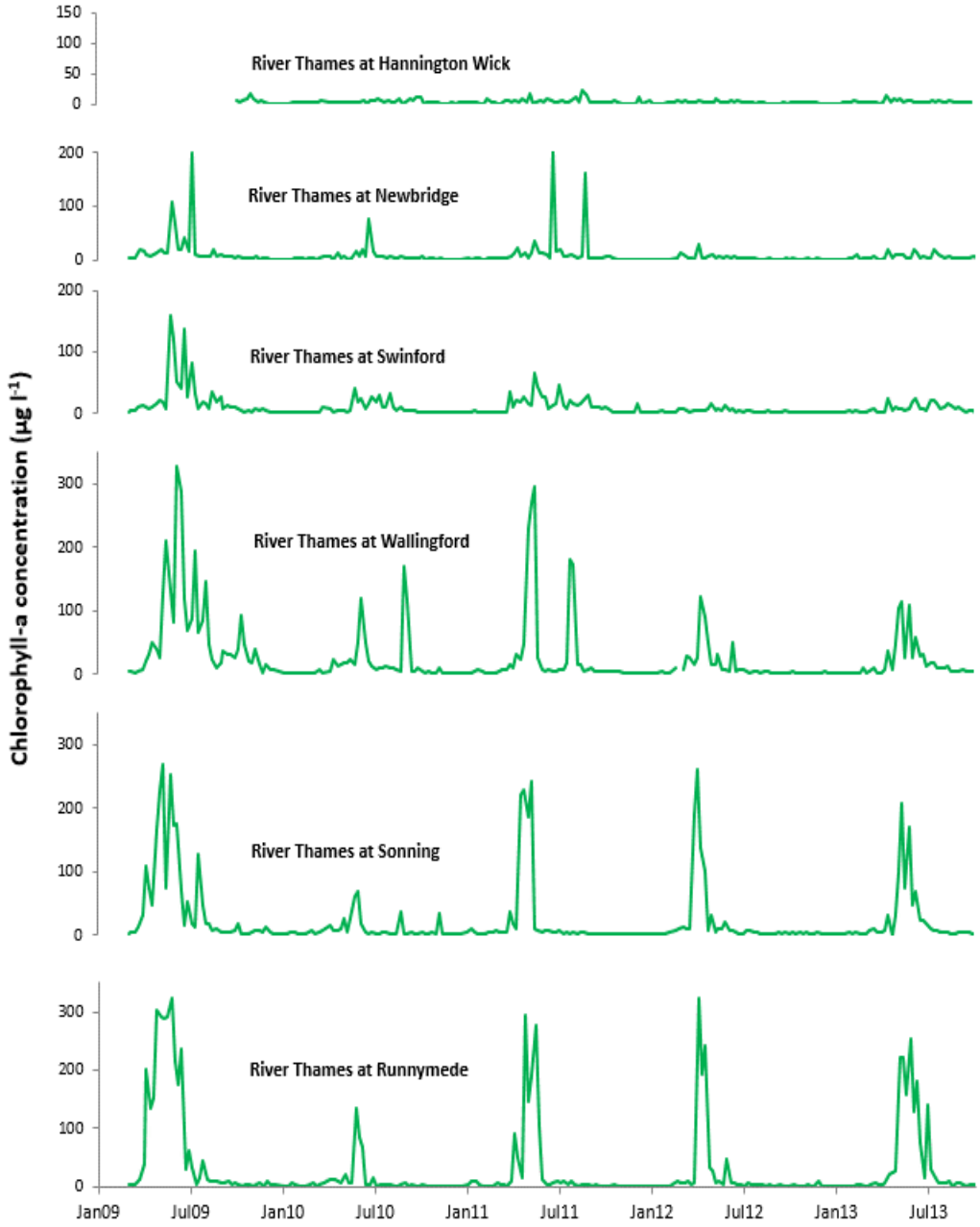


Figure 2. Chlorophyll concentrations along the River Thames (Feb 2009 to September 2013), based on weekly observations.

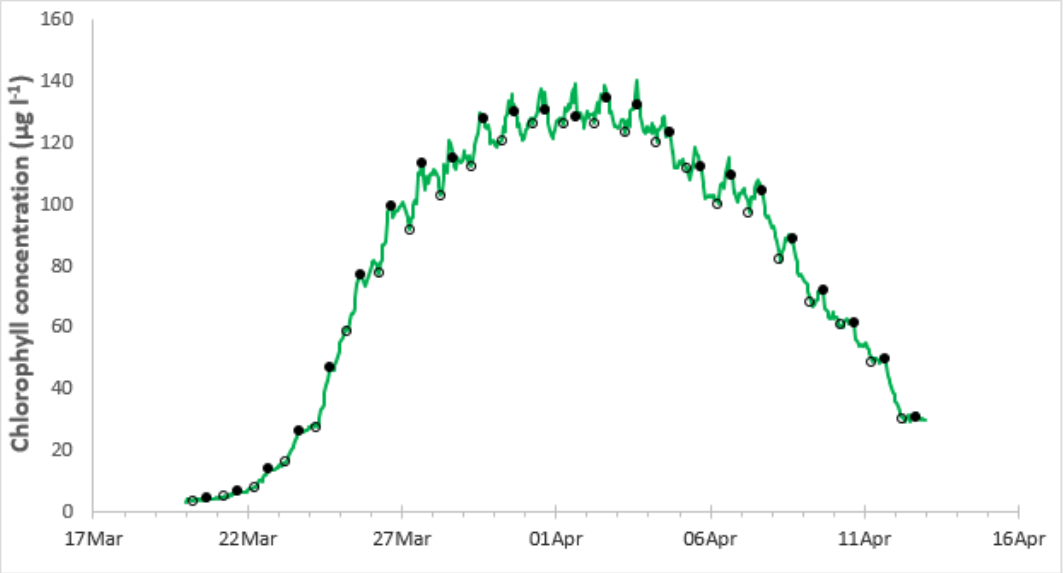
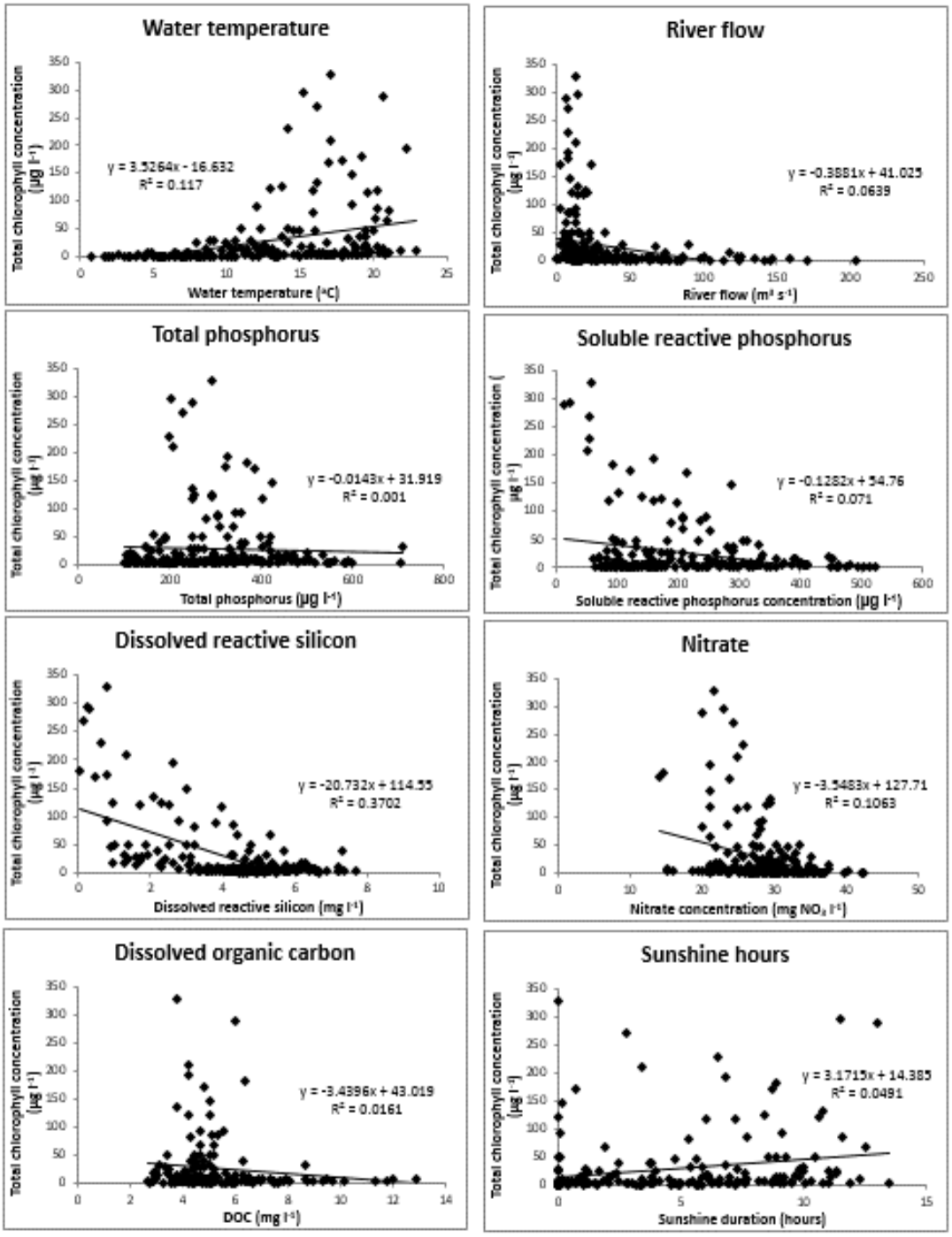


Figure 3. Hourly chlorophyll concentration data for the River Thames at Reading in 2012, showing diurnal cycling during the phytoplankton bloom. Filled black circles = samples taken at 16:00h, Open circles = samples taken at 06:00h.



Supplementary Figure 1. Chlorophyll-a concentration relationships with water temperature, river flow, nutrient concentrations and light for the River Thames at Wallingford, based on weekly observations from 2009 to 2013.

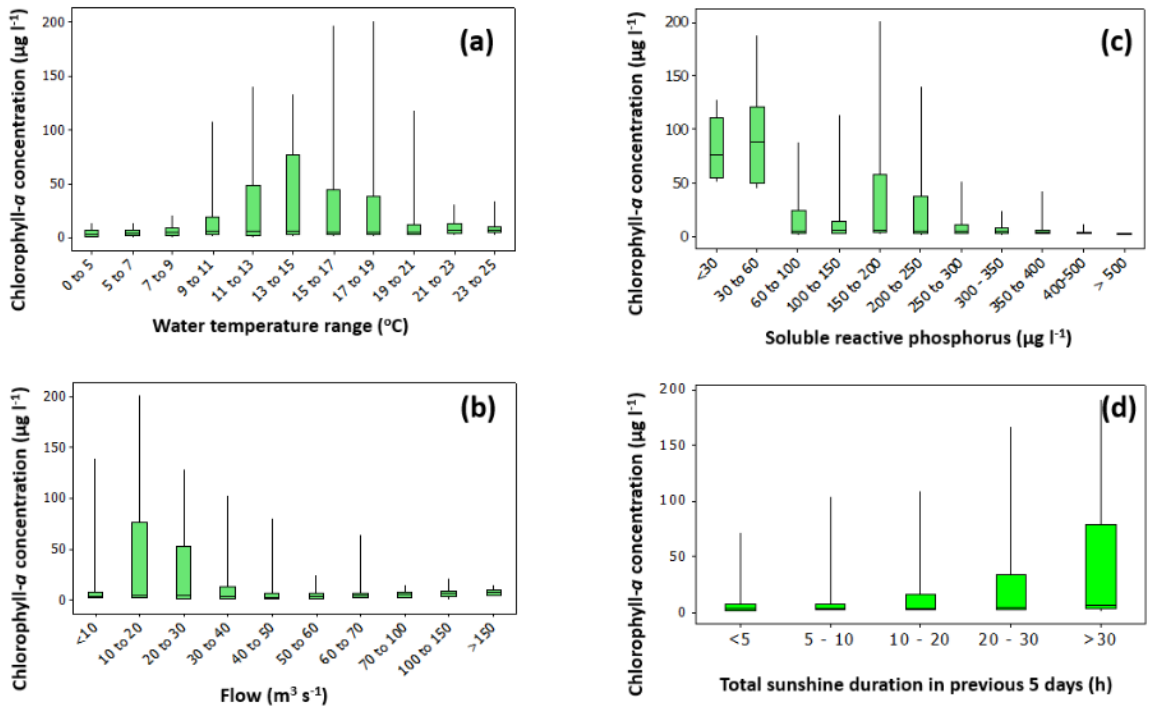


Figure 4. Boxplots of hourly chlorophyll-a concentration data for the River Thames at Reading and (a) hourly water temperature (Reading), (b) hourly average flow (Reading) and (c) weekly soluble reactive phosphorus concentrations (Wallingford) from February 2009 to September 2013. Box represents 10th to 90th percentile. Line within each box denotes the mean chlorophyll concentration.

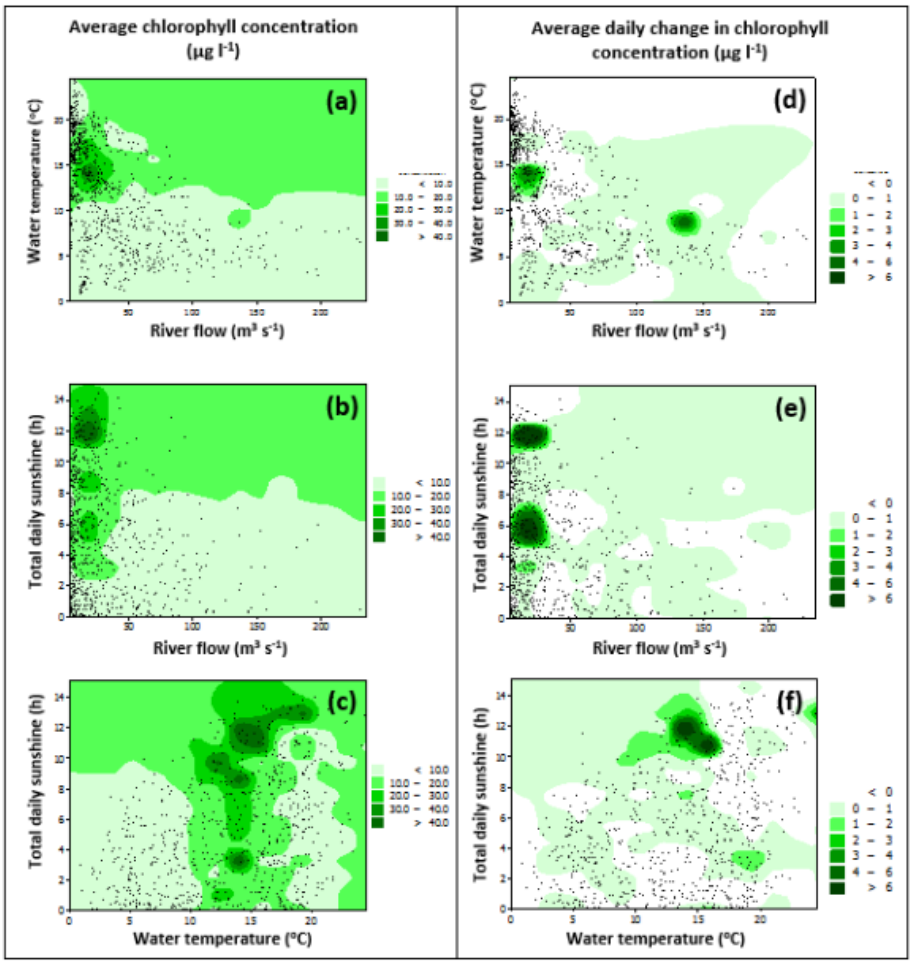


Figure 5. Multiple stressor relationships between phytoplankton growth (measured by (a-c) daily chlorophyll concentrations and (d-f) average daily change in chlorophyll concentrations) and daily water temperature and flow of the Thames at Reading and the total number of hours of sunshine (measured at CEH Wallingford meteorological site). Chlorophyll, water temperature and flow observations taken at 12 noon were used for this analysis.

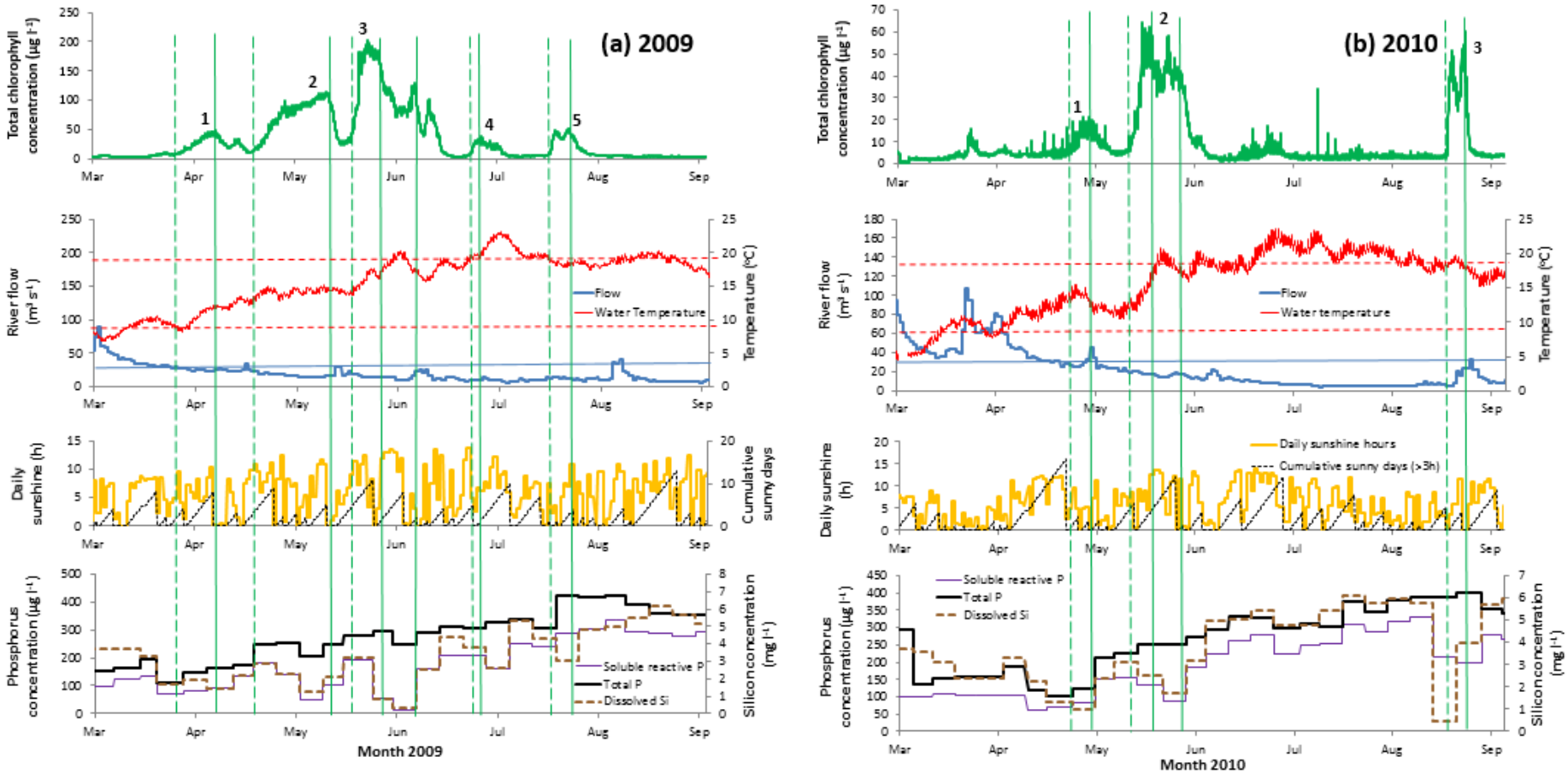


Figure 6. Chlorophyll, water temperature and flow time series data for the River Thames at Reading, and daily sunshine hours and weekly nutrient data from Wallingford. Horizontal lines indicate threshold values for temperature (red) and flow (blue). Vertical green lines indicate starts of periods of chlorophyll increase (dashed lines) and decrease (solid lines).

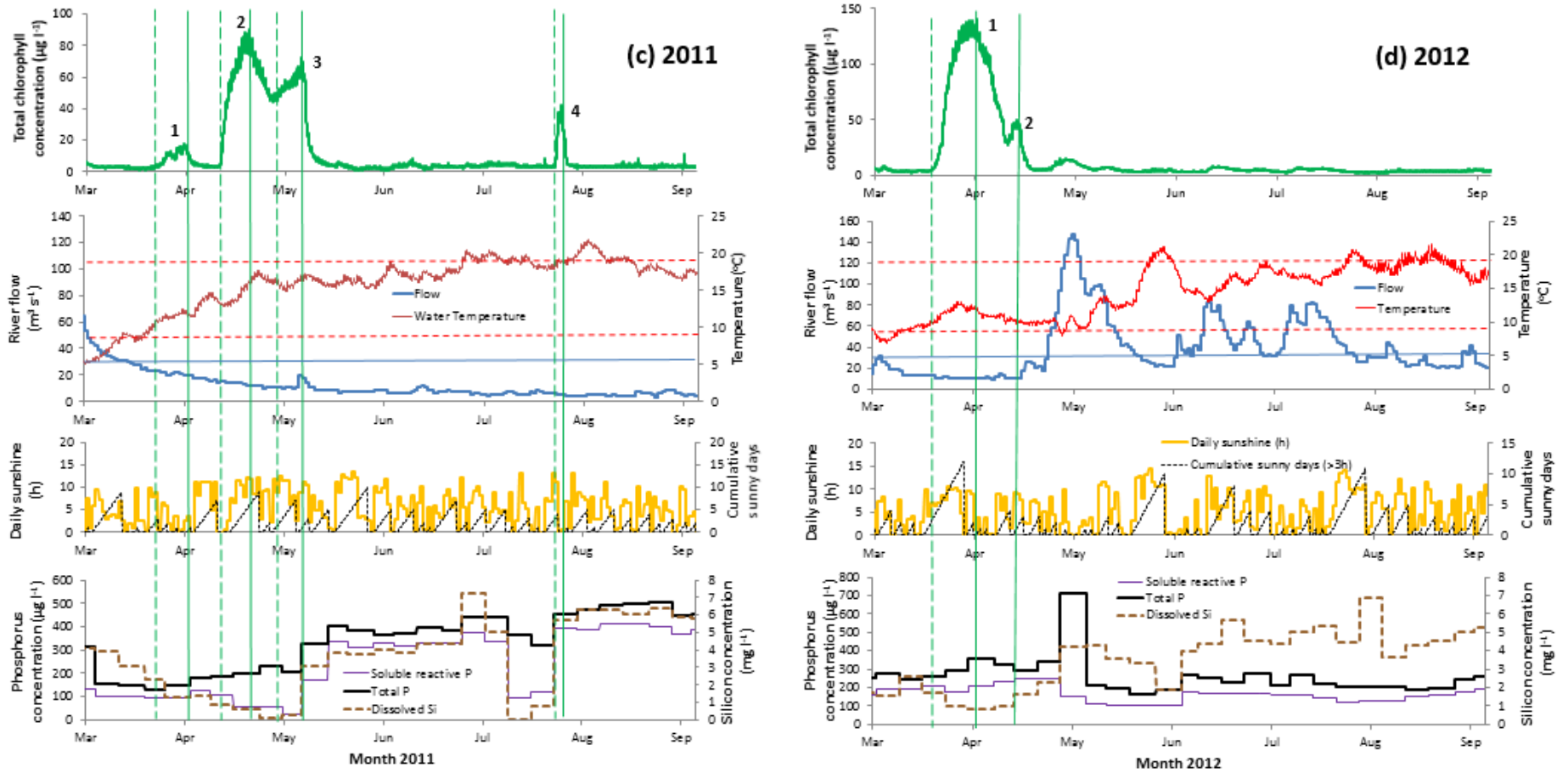


Figure 6 (continued). Chlorophyll, water temperature and flow time series data for the River Thames at Reading, and daily sunshine hours and weekly nutrient data from Wallingford. Horizontal lines indicate threshold values for temperature (red) and flow (blue). Vertical green lines indicate starts of periods of chlorophyll increase (dashed lines) and decrease (solid lines)

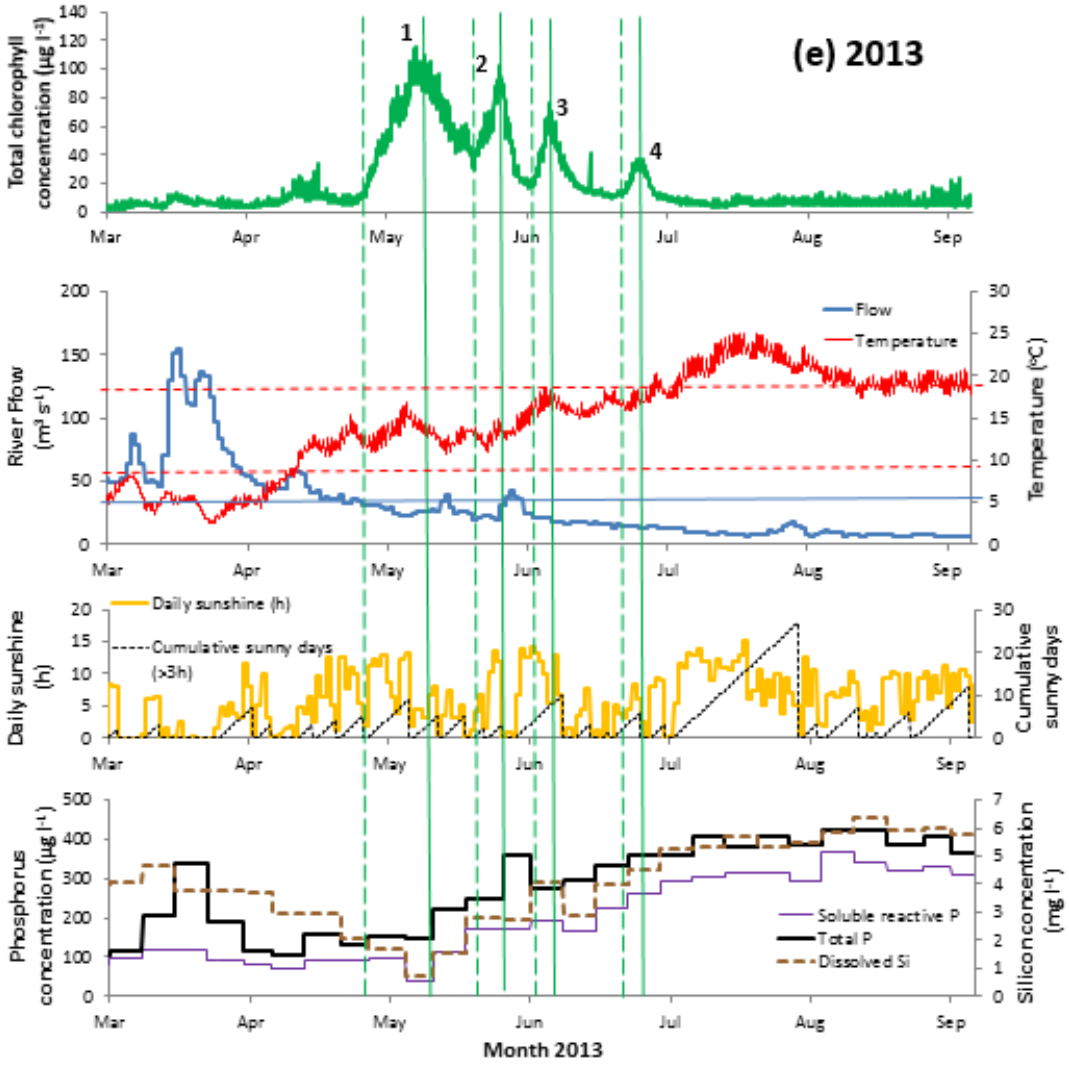


Figure 6 (Continued). Chlorophyll, water temperature and flow time series data for the River Thames at Reading, and daily sunshine hours and weekly nutrient data from Wallingford. Horizontal lines indicate threshold values for temperature (red) and flow (blue). Vertical green lines indicate starts of periods of chlorophyll increase (dashed lines) and decrease (solid lines)