Bowes, Michael J.; **Palmer-Felgate, Elizabeth J.**; **Jarvie, Helen P.**; Loewenthal, Matthew; **Wickham, Heather D.**; **Harman, Sarah A.**; **Carr, Emily**. 2012 High-frequency phosphorus monitoring of the River Kennet, UK: are ecological problems due to intermittent sewage treatment works failures? *Journal of Environmental Monitoring*, 14 (12). 3137-3145. 10.1039/c2em30705g

High-frequency phosphorus monitoring of the River Kennet, UK: Are ecological problems due to intermittent sewage treatment works failures?

Michael J. Bowes,*[a] Elizabeth J. Palmer-Felgate[a], Helen P. Jarvie[a], Matthew Loewenthal[b], Heather D. Wickham[a], Sarah A. Harman[a] and Emily Carr[a].

[a] *Centre for Ecology and Hydrology, Maclean Building, Benson Lane, Crowmarsh Gifford, Wallingford, UK.*

Fax: +44 1491692424; Tel: +44 1491838800*; E-mail:mibo@ceh.ac.uk*

[b] *Environment Agency, Fobney Mead, Rose, Kiln Lane, Reading, Berkshire RG2 0SF, UK*

Abstract

The River Kennet in southern England has exhibited excessive benthic algal growth and associated ecological problems, such as loss of macrophytes and invertebrates, since the 1980s. These ecological problems were attributed to regular peaks in phosphorus concentration, which were widely attributed to intermittent failures of the Marlborough sewage treatment works (STW). This study deployed high-frequency phosphorus auto-analysers to monitor the total reactive phosphorus (TRP) concentrations of Marlborough STW final effluent and the downstream River Kennet at hourly and 30 minute resolution respectively, between 2008 and 2009. This monitoring confirmed that the Marlborough STW was operating well within its 1000 μg l^{-1} annual mean total phosphorus consent limit, with mean total P and soluble reactive P concentrations of 675 and 345 μg l^{-1} respectively. There were two occasions where effluent TRP concentration exceeded 1000 μg l^{-1}, and only one of these resulted in a peak in TRP concentration of over 100 μg l^{-1} in the River Kennet at Mildenhall. The other nine peaks of over 100 μg l^{-1} in the River Kennet during the monitoring period were associated with storm events, indicating that diffuse-source inputs and remobilisation of stored within-channel phosphorus were the cause of the peaks in river concentration, rather than Marlborough STW. The value of high-frequency environmental monitoring and the problems associated with using

nutrient auto-analysers in the field are discussed. Seasonal phosphorus consents for STWs could provide a useful and cost effective means to improve both water quality and river ecology in the upper River Kennet.

Key words

Eutrophication; phosphorus; effluent; Chalk stream; *in-situ* monitoring; high-frequency.

1 Introduction

Elevated river nutrient concentrations have been shown to cause reductions in ecological status, often resulting in excessive phytoplankton and periphyton growth, and can lead to the loss of plant, invertebrate and fish communities [1-3]. Across Europe, much effort is being focussed on reducing nutrient (and in particular phosphorus (P)) loadings to rivers in recent years, in an effort to comply with the European Union's Water Framework Directive. This has been tackled by introducing improved sewage treatment processes [4], and changing agricultural practices and land use to reduce diffuse-source inputs [5-6].

It is imperative that the relative contributions from point and diffuse sources of phosphorus are known for a given catchment, so that resources can be most effectively targeted to reduce trophic status and improve aquatic ecology. A range of source apportionment methodologies have been developed to determine the relative loads from sewage and agriculture, using standard water-quality datasets [7-10], sewage tracers such as boron [11-12] and land use data [13-15]. However, using these existing standard water-quality datasets (which are often monthly sampling interval, or, at best, weekly), it is difficult to identify the presence of sporadic nutrient pollution episodes [16], and very difficult to establish the source of these phosphorus peaks. These largely-undetected, short-duration periods of elevated phosphorus concentration could be having a major impact on river ecology [17]. If episodic peaks in P concentration are occurring in rivers, phosphorus analysis at sub-daily resolution would be required to determine both the magnitude and duration of these peaks [18-19]. Analytical field monitors are now becoming commercially available, which will allow this high-frequency phosphorus monitoring of rivers at a resolution required to identify the presence of such pollution incidents [19-21].

The River Kennet in southern England has exhibited excessive benthic algal growth and associated ecological problems, such as loss of macrophytes and invertebrates, since the 1980s [22-23]. To try to improve river ecology, phosphorus removal was introduced at all large sewage treatment works (STW) discharging into the River Kennet, resulting in a 72% reduction in SRP concentration from ca. 548 µg l^{-1} to 126 µg l^{-1} in the upper reaches of the river, downstream of the town of Marlborough, in the late 1990s [24]. Despite this major improvement in water quality (and others throughout the 2000s, due to the introduction of more stringent STW phosphorus consents [25]), excessive benthic periphyton growth has persisted. Weekly water quality monitoring during the early 2000s highlighted that there were regular peaks in phosphorus concentration in the upper Kennet, and these peaks appeared to be correlated to the occurrence of epiphytic algal blooms. It was postulated that the ecological system had become sensitised, following the reduction in phosphorus loading, and these peaks in soluble reactive phosphorus concentration (above 100 µg l^{-1}) could be sustaining the high periphyton biomass present in stretches of the upper Kennet [26]. The Marlborough STW was implicated as the most likely source of these episodic phosphorus peaks[27].

This study aimed to use in-situ, high frequency nutrient auto-analysers to determine if these regular peaks in phosphorus concentration were still occurring in the upper River Kennet in 2008-2009, and if so, what were their frequency, magnitude and duration. This study also aimed to determine if peaks in river phosphorus concentration coincided with peaks in the P concentration of the final effluent from Marlborough STW, thereby establishing if they were caused by intermittent failures of the sewage treatment process, or were related to river flow, which would imply that the source of the phosphorus spikes was due to diffuse inputs. Additional weekly monitoring was employed in the upper Kennet catchment to identify if peaks in river phosphorus concentration downstream of Marlborough STW originated in the headwaters.

1.1 Study area

The River Kennet is one of the largest tributaries of the River Thames, with a total catchment area of *ca*. 1200 km^2 (Figure 1). It rises near the village of Avebury in Wiltshire, and flows in a southerly, then easterly direction to discharge into the River Thames at the town of Reading, ca. 30 km west of London. The land use of the upper River Kennet is predominantly grassland and arable. The only significant town in the upper catchment is Marlborough, served by a STW (population estimate = 9250) employing phosphorus removal by iron dosing. There are also two STW at Fyfield (population estimate of 1580) and Broad Hinton (population estimate of 540), serving some of the dispersed villages in the upper Kennet catchment. The catchment geology is principally Cretaceous Chalk, and therefore the River Kennet is predominantly groundwater fed, with a very high baseflow index of 0.94 at Marlborough [28]. A more detailed description of the River Kennet catchment can be found elsewhere [27, 29].

This study employed high frequency monitoring of the final effluent stream of the Marlborough STW (grid reference SU200693) and the River Kennet at the village of Mildenhall (grid reference SU212694), approximately 2 km downstream of the sewage treatment works. Previous studies had shown the presence of intermittent spikes in phosphorus concentration in the Kennet at Mildenhall in the early 2000s [26], and subsequent high frequency (hourly) monitoring in 2004 to 2006 showed that there were still substantial phosphorus peaks occurring [20]. This section of the river was particularly badly affected by excessive benthic algal growth, and the majority of the river bed was covered in a thick layer of periphyton throughout the spring to autumn period in both 2008 and 2009. The study reach had very low macrophyte biomass (mainly *Callitriche platycarpa*) and an almost complete absence of *Ranunculus*; a key macrophyte for chalk rivers. The river width at Mildenhall was 9 m, and average depth was 0.5 m. The mean annual river flow at the site (from 1972 to 2005) was 1.2 $m^3 s^{-1}$, with an annual average rainfall at Marlborough of 828 mm [28]. The River Og tributary enters the River Kennet ca. 300 m upstream of the STW discharge point. The River Og catchment is almost entirely rural, with a few dispersed small villages, and has no STW discharges. The mean annual flow of the River Og was 0.32 $m^3 s^{-1}$.

2 Methodology

2.1 High frequency phosphorus monitoring

Two high-frequency phosphorus auto-analysers were installed within insulated metal cabinets adjacent to the River Kennet at Mildenhall and the final effluent discharge channel of Marlborough sewage treatment works. The total reactive phosphorus (TRP) concentration (determined using the same methodology as for soluble reactive phosphorus analysis, but carried out on an unfiltered, rather than a filtered sample) of the River Kennet at Mildenhall was monitored using a Systea Nutrient Probe Analyser (Systea, Anagni, Italy). The river was monitored at a 30 minute sampling interval, to allow short-duration pollution incidents to be detected, and their duration and maximum concentration to be quantified. The monitoring period extended from the 31st March 2008 to 24th August 2009. Further details of the monitoring infrastructure at this study site and operation of the Nutrient Probe Analyser can be found in Palmer-Felgate et al., (2008). The TRP concentration of the Marlborough STW final effluent was monitored at hourly interval from 8th June 2008 to the 13th August 2009, using a Systea Micromac-C auto-analyser (Systea, Anagni, Italy). Samples were taken from the final effluent channel, just before it discharged into the River Kennet.

The Nutrient Probe Analyser and the Micromac C auto-analysers both operate in a similar manner. Both instruments use an internal peristaltic pump to take a sample of water through a 1.5 mm internal diameter black (to exclude light and minimise algal growth) vitron tubing, positioned in the main flow of the river channel or effluent stream. A pre-filter unit, consisting of a 1 mm mesh inlet was attached to the end of the sample tube, to stop large particles of debris entering (and potentially blocking) the instruments' colorimetry system. The TRP concentration of each sample was quantified by spectrophotometry, using a modified version of the method of Murphy and Riley [30]. Each instrument carried out a daily self-check, using a quality control check-standard, to confirm that they were operating correctly. In addition, the instruments were visited every two weeks, to carry out a calibration and instrument check, general maintenance, and to renew the chemical reagents and check-calibration standards.

The raw, high-frequency data were processed using WISKI (Water Management Information System; Kisters Inc., California, USA) to remove negative data and outliers that consisted of a single data point. These spurious data points are common when using this type of auto-analyser, and can be caused by a variety of problems, such as the presence of air bubbles within the spectrophotometer cuvette, or sample line blockages resulting in sampling failure. This removal of 'single' peaks from the data set was considered justified, as it was assumed that a STW failure would last longer than 1 hour (especially as the Marlborough STW is largely unmanned). Also, any large, short-duration phosphorus peak that was discharged from the STW would become a broader, longer-duration peak by the time it had been transported to Mildenhall, due to advection / dispersion processes, and so the 30 minute monitoring interval at Mildenhall would pick up multiple points through the pollution incident.

2.2 Manual water quality sampling

Water samples were collected by the Environment Agency from the River Kennet at Clatford and Mildenhall (upstream and downstream of the town of Marlborough), and from the final effluent stream of Marlborough STW (Figure 1), at weekly intervals between 11th March 2008 and 27th October 2009 [25]. Additional samples were taken by the Centre for Ecology and Hydrology at fortnightly intervals from Marlborough STW final effluent and the River Kennet at Mildenhall, and these data were directly used to check the data generated by the high-frequency auto-analysers. Samples from the River Og at Poulton Farm (50m from the confluence with the River Kennet) were also taken at fortnightly intervals to confirm that peaks observed in the Kennet at Mildenhall were not due to phosphorus pollution incidents within the River Og catchment.

Aliquots of these water samples were immediately filtered in the field through a 0.45 µm cellulose nitrate filter membrane (Whatman International Ltd., Maidstone, UK). The samples were returned to the Centre for Ecology and Hydrology's nutrient laboratory for analysis. The unfiltered and filtered samples were analysed for total phosphorus (TP) and total dissolved phosphorus (TDP respectively, by digesting 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 [31]. The filtered water samples were also analysed for SRP concentration. SRP was determined spectrophotometrically, using an adapted phosphomolybdenum blue method [30, 32].

3 Results and discussion

The high-frequency TRP concentration data from the River Kennet at Mildenhall and Marlborough STW final effluent are shown in Figure 2. There are numerous data gaps, due to regular instrument breakdown. Most of these were caused by fouling and blockages of the sample intake pipe and instrument valves by river algae / debris, particularly when sampling final sewage effluent. There were also problems associated with pipes freezing during the winter period. Despite these problems, the Systea instruments provided periods of good-quality high-frequency data that were in close agreement with the phosphorus data obtained from the manual sampling / traditional laboratory analysis. The high-frequency TRP data for the River Kennet at Mildenhall covered five of the ten high-flow storm events observed during the monitoring period (Figure 2). The other five high-flow events were captured by manual sampling.

3.1 Phosphorus concentrations of Marlborough STW final effluent.

The monitoring programme confirmed that the Marlborough STW was operating well within its mean annual total phosphorus consent limit of 1000 µg l^{-1} between March 2008 and September 2009, with a mean SRP concentration (based on the manual sampling data) of 345 µg l^{-1} and a mean TP concentration of 675 µg l^{-1} (Table 1). The high-frequency auto-analyser data consistently produced TRP results that were on average ca. 30 % higher than the corresponding SRP concentration from the manual sampling (Figure 2A). This indicates that the final sewage effluent consists of a large proportion of suspended, colloidal phosphorus-rich particles, greater than 0.45 µm in diameter. The proportion of the mean total phosphorus concentration that was in the form of SRP was 51 %, which is much lower than has been observed in other UK STW effluent studies [33-34]. This increase in effluent particulate phosphorus is probably directly due to the iron dosing of the effluent, resulting in precipitation of the dissolved phosphorus coming from the secondary sewage treatment process.

The high-frequency auto-analyser monitoring identified only two periods where the TRP concentration exceeded 1000 µg l^{-1}, in September 2008 (exceeding 1000 µg l^{-1} for a period of 3 days, and reaching a maximum of 1410 µg l^{-1}; peak L in Figure 2A) and March 2009 (exceeding 1000 µg l^{-1} for 21 days and reaching a maximum of ca. 1300 µg l^{-1}; Peak M in Figure 2A). There were also two additional peaks in the SRP concentration of over 800 µg l^{-1} identified from the manual sampling data, on 20th April 2008 and 24th August 2009 (labelled as peaks K and N respectively in Figure 2A), during periods of auto-analyser breakdown. The other sporadic, high-resolution phosphorus peaks (particularly occurring in September 2008 and June 2009) consisted of only two to three data points, and were considered to be instrument noise, based on the shape and short duration of the peaks, and the lack of corroborative evidence from the manual sampling data.

Peaks in effluent P concentration did not correlate with the typical short-term storm events (as indicated by the mean daily flow of the River Kennet at Mildenhall (Figure 2C)), showing that the Marlborough STW was able to cope with periods of high rainfall during the monitoring period. However, the sustained increase in P concentration in March 2009 (peak M, Figure 2A) coincided with a long period of sustained rainfall and high river flow, and may indicate that under these conditions of high volumetric throughput, the STW was less effective at P removal, or may indicate that untreated sewage was being released as a combined sewer overflow.

3.2 Phosphorus concentrations in the River Kennet at Mildenhall.

The combined phosphorus concentration results from the high-frequency auto-analyser and manual sampling are shown in Figure 2B. The auto-analyser TRP results from the River Kennet at Mildenhall were very similar to the SRP data generated from the laboratory analysis of the manual samples (Figure 2B), confirming that the Systea auto-analyser produced accurate and reliable results throughout the monitoring period. The mean TRP concentrations throughout the monitoring period were 2 % higher than the mean SRP concentrations, showing that there was little colloidal reactive-phosphorus within the river water column.

The average SRP and TP concentrations during the monitoring period (based on weekly manual sampling data) was 67 μg l^{-1} and 110 μg l^{-1} (Table 1). This exceeded the 50 μg l^{-1} SRP annual target for 'High' water quality status for chalk streams, but would still be classified as 'Good', in terms of phosphorus concentration [35]. There has been a ca. 80 % reduction in mean annual SRP and TP concentration of the River Kennet at Mildenhall since 1997, when the average and maximum SRP concentrations were 390 and 690 μg l^{-1} respectively [36]. There has been a continuing improvement in recent years, with the annual mean SRP concentration in both 2008 and 2009 being lower than any year since 1997 (Table 2). These improvements in P concentration across the River Kennet have been directly attributable to improvements in sewage treatment [25]. Despite the decrease in annual average SRP concentration to the border of Good and High water quality [35], the intermittent peaks in SRP concentration observed in previous studies of the River Kennet [20, 26] were still occurring. Three of the peaks were in excess of 200 μg l^{-1}, and there were eight periods where SRP concentration exceeded 100 μg l^{-1}; a threshold concentration that was suggested by Jarvie et al (2004) as a trigger for excessive epiphytic algal growth. Most of these phosphorus peaks were of relatively short duration. The high frequency TRP monitoring data allowed the size and duration of these peaks to be quantified. Most peaks lasted between three and five days (peaks b, c, d, f and n; Figure 2B). There were also two more-sustained SRP peaks of 10 days duration (peaks L and i; Figure 2B).

3.2.1 Causes of TRP and SRP peaks in the River Kennet

The majority of the SRP and TRP concentration peaks observed in the river coincided with storm events. The daily mean flow hydrograph of the River Kennet at Mildenhall is presented in Figure 2C, highlighting the ten largest flow peaks throughout the monitoring period (peaks a-j; Figure 2C). Eight of these ten storm events coincided with a peak in SRP and/or TRP concentration. The highest P concentrations were observed in June and November 2008, and coincided with flow peaks c, e and f (Figure 2B). These storm events followed 3-4 month periods of dry antecedent conditions. During these dry periods, phosphorus would have accumulated along the floodplain, and also within the river channel itself, due to deposition of phosphorus-rich sediment and sequestering of dissolved phosphorus from the water column by fine bed-sediments and riverine biota. The rainfall and increased river flow velocity associated with these storm events would have mobilised this accumulated floodplain and bed-sediment phosphorus into the water column, and released P-rich sediment pore waters into the water column, resulting in phosphorus concentration peaks in the river. Similar observations have been made in previous studies [37-39]. The three largest storm events (peaks a, g and i; Figure 2C) all produced SRP concentration peaks of over 100 µg l^{-1} in the River Kennet at Mildenhall, and these did not correlate to phosphorus peaks in the Marlborough STW final effluent. However, the Marlborough STW could be a source of P to the river, due to combined sewer overflows (CSO). These storm events would deliver large quantities of water to the STW, via the road drainage network, and may result in the excess raw sewage to be delivered directly to the river.

The most sustained storm event was in February 2009 (peaks i-j; Figure 2C), and resulted in a two month period of high flows. This coincided with one of the longer-duration SRP peaks, lasting ten days. This shows that sustained periods of high flow and associated rainfall produces phosphorus peaks that have a longer duration. However, the high SRP concentrations in the river were not sustained throughout the period of increased river flow, which indicates that the labile and easily mobilised phosphorus stored both on the floodplain and within the river channel is quickly depleted from the system. Evidence for this depletion is further shown during storm peak j, which has no effect on river P concentration (Figure 2B).

There was one major TRP and SRP peak that occurred in September 2008 that was not associated with a storm event. The peak reached a maximum concentration of 137 µg l^{-1}, and lasted for nine days duration (Figure 2B). This coincides with the SRP and TRP peak in the Marlborough STW final effluent (1410 µg TRP l^{-1}) (peak L; Figure 2A), which strongly suggests that this pollution incident was caused by an intermittent failure of the Marlborough STW. There was also a phosphorus peak in the River Kennet at Mildenhall in August 2009 (maximum TRP of 106 µg l^{-1}; peak N; Figure 2A) that coincided with another peak in SRP concentration in the STW effluent of 842 µg l^{-1} (although this is well within Marlborough STW's consent limit of 1000 mg l^{-1} annual average). The longest period of increased phosphorus concentration in the STW effluent occurred throughout March 2009 (peak M; Figure 2A), reaching a maximum TRP concentration of ca. 1300µg l^{-1}. This did not result in any increase in SRP concentration in the River Kennet. This is probably due to the increased river flow at this time, which would dilute the incoming sewage effluent. This highlights the possible effectiveness of seasonal consent limits for STWs. Resources (i.e. iron dosing rates) could be focussed on removing phosphorus during low flow periods during the biologically-active March to September period, and relaxed during periods of high river flow when effluent dilution will be significant, and particularly during the ecologically less-sensitive winter period, although the impact of seasonal STW consents on phosphorus dynamics and river ecology would need to be fully investigated before such a practice was widely adopted.

3.2.2 Catchment phosphorus sources

The TP and SRP concentration data from the manual sampling programme are shown in Figure 3. This shows that most of the storm-related phosphorus peaks observed at Mildenhall also occur in the upper River Kennet and River Og (peaks a, c, d, e, f, g and i). This confirms that the major phosphorus source during periods of rainfall is probably from a combination of diffuse inputs from across the catchment (from agriculture and septic tanks discharging to soak-aways) and remobilisation of stored phosphorus from within the river channel itself, rather than an increasing phosphorus load from the Marlborough STW. The monitoring of the Marlborough STW final effluent confirmed that the SRP and TRP concentrations do not increase during storm events, but the SRP and TRP loads to the river could have increased dramatically, due to increased volumetric flow rates as the STW receives large amounts of storm water from road drains. During the larger storm events, CSOs from Marlborough STW are also likely to contribute to the peaks observed in the River Kennet at

Mildenhall. However, as phosphorus peaks are also observed in the upper Kennet at Clatford, and the River Og (which has no sewage treatment works within its catchment), this infers that diffuse inputs and within-river remobilisation are primarily responsible for the observed peaks in phosphorus concentration within the River Kennet during storm events.

Some P peaks are very small in the upper catchments, compared to the peaks observed in the River Kennet at Mildenhall (e.g. peak c at Clatford, peak i on the River Og). To a large extent, this is probably due to the relatively low frequency of sampling. Pollution spikes in the headwater catchments are likely to be of relatively short duration, but will broaden as they travel downstream, due to advection and dispersion processes [40]. Therefore, the phosphorus peaks are more likely to be observed at the River Kennet at Mildenhall, but these peaks could easily be missed at the headwater sites. This highlights the need to adopt high-frequency auto-analyser technology for effective monitoring of rivers, to gain insights into how these systems are operating.

The TP data confirms that the Marlborough STW had four periods of high effluent phosphorus concentration (peaks K, L, M and N; Figure 3C). The discharges in May 2008 (peak K) and March 2009 (peak M) had no effect on either the weekly manual TP or SRP concentrations in the River Kennet at Mildenhall. The peaks in effluent P concentration in September 2008 (peak L) and August 2009 (peak N) did result in small peaks in SRP and TP concentration in the River Kennet at Mildenhall, reaching TP concentrations of 133 μg l^{-1} and 177 μg l^{-1} respectively, and SRP concentrations in excess of 100 μg l^{-1}. This is probably due to these effluent peaks occurring at times of low river flow, and so dilution of STW effluent would be it its minimum. There are no corresponding peaks in P concentration in the upper Kennet at Clatford or the River Og, indicating that Marlborough STW is probably the source. These STW-related peaks are relatively small, in comparison to those associated with diffuse inputs during major storm events, but they are still important, as they are easier to control (compared to agricultural diffuse pollution) and are more likely to occur during low flow periods within the biologically-active growing season.

4 Conclusions

This paper has demonstrated the usefulness of the high-frequency phosphorus data produced by nutrient auto-analysers in determining the presence, magnitude and duration of intermittent phosphorus pollution incidents in rivers, and their potential sources. It also highlights the difficulties in producing continuous data from environmental samples using these auto-analyser instruments in the field, despite the infrastructure and methodologies developed within this project. The supporting manual sampling (approximating to weekly sampling interval or better) was sufficient in this case to capture the majority of the pollution incidents, but gave no information on magnitude and duration of peaks. Monthly sampling interval (typical of most water quality monitoring programmes in the UK) would have missed most of the phosphorus peaks, showing the severe limitations of this monitoring for detecting pollution incidents.

The high-frequency monitoring data show that the peaks in phosphorus concentration observed in studies throughout the 2000s still occurred, although their size and frequency were now lower than those observed in the early 2000s [20, 26]. Almost all of these peaks were associated with storm events, indicating that the source of phosphorus pollution was from diffuse inputs from the upper catchment and remobilisation / desorption of stored phosphorus from within the river channel itself, rather than intermittent STW failures, although CSO discharges from the STW will also contribute to these peaks in river phosphorus concentration.

The monitoring of Marlborough STW's final effluent confirmed that the STW was operating well within its consent level of an annual average phosphorus concentration of 1000 µg l^{-1}. There were two periods where effluent P concentration were greater than 1000 µg l^{-1}, and only one of these (during the period of low river flow in September 2008) resulted in a peak in SRP concentration in the River Kennet at Mildenhall. The sustained period of high effluent SRP concentration in March 2009 (with a maximum SRP concentration of 1300 µg l^{-1} SRP and with concentrations greater than 1000 µg l^{-1} for a period of 21 days) had little effect on river phosphorus concentrations, due to dilution by the high river flows at the time. This shows that phosphorus effluent consents could potentially be relaxed during high-flows, particularly in winter, without risk to the ecological status of the River Kennet, although further research would be required to confirm this.

A previous nutrient-limitation study in the River Kennet at Mildenhall showed that increasing river SRP concentration from ca. 60 µg l^{-1} to 170 µg l^{-1} for a period of 9 days had no effect on biofilm growth rate, which strongly indicates that these phosphorus peaks are not responsible for the excessive benthic algal growth that exists at the site [41]. This nutrient limitation study also demonstrated that reducing the SRP concentration of the River Kennet at Mildenhall to below 50 µg l^{-1} during the growing season reduced the rate of periphyton growth [41]. Therefore, the typical average SRP concentrations during the spring and summer need to be reduced to decrease periphyton growth rate and potentially improve ecological status of the upper Kennet, rather than trying to prevent the intermittent spikes in phosphorus concentration.

This study has shown that the Marlborough STW was not responsible for the great majority of phosphorus concentration peaks observed in the River Kennet at Mildenhall, or directly for the excessive periphyton growth that occurs in this part of the upper Kennet. However, implementing a seasonal discharge consent system for the STW, focusing on further reducing effluent phosphorus concentrations in spring and summer, and relaxing consents during winter high-flow periods, could be the most effective way of controlling excessive benthic algal growth in the upper Kennet. However, it is important to note that reductions in phosphorus concentration are not the only way to control benthic algal growth in rivers. Increasing flow velocity by removing weirs and sluices (and thereby reducing residence times) [42], providing riparian shading [43-44], and establishing a more natural and diverse foodweb which promotes invertebrate grazers could have a much greater impact on controlling biofilm development than nutrient reduction alone, and these should also be considered as potential mitigation strategies by catchment managers.

Acknowledgements

This work was funded by the Natural Environment Research Council. We thank Ellie Martin and John Hallett of the Environment Agency for providing water quality data. We are very grateful to John Hounslow (Action for the River Kennet) for allowing the installation of monitoring equipment at Mildenhall, and for sharing his great knowledge of the catchment, and to Thames Water for allowing access to Marlborough sewage treatment works. River flow data was supplied by the National River Flow Archive.

Table 1. Summary phosphorus concentration statistics for the River Kennet, River Og and the final effluent of the Marlborough sewage treatment works. Results based on data from a weekly manual sampling programme.

Determinand		Marlborough STW final effluent	River Kennet at Mildenhall	River Kennet at Clatford	River Og at Poulton Farm
Soluble reactive P (μg l^{-1})	Mean	345	67	69	34
	Maximum	1104	341	444	151
	Minimum	80	19	20	3.5
	Number of data points	113	117	82	34
Total dissolved P (μg l^{-1})	Mean	410	85	82	46
	Maximum	1166	387	586	171
	Minimum	127	47	32	3.5
	Number of data points	112	116	82	33
Total P (μg l^{-1})	Mean	675	110	96	62
	Maximum	1416	495	697	217
	Minimum	205	35	37	15
	Number of data points	113	117	82	34

Year	Soluble reactive P (μg l^{-1})	Total P (μg l^{-1})
1997	390	465
1998	86	129
1999	94	146
2000	95	144
2001	90	150
2002	84	126
2003	69	101
2004	74	103
2005	97	130
2006	78	121
2007		
2008	67	112
2009	66	106

Table 2. Mean annual soluble reactive phosphorus and total phosphorus concentrations for the River Kennet at Mildenhall. Data taken from Neal et al., [36].

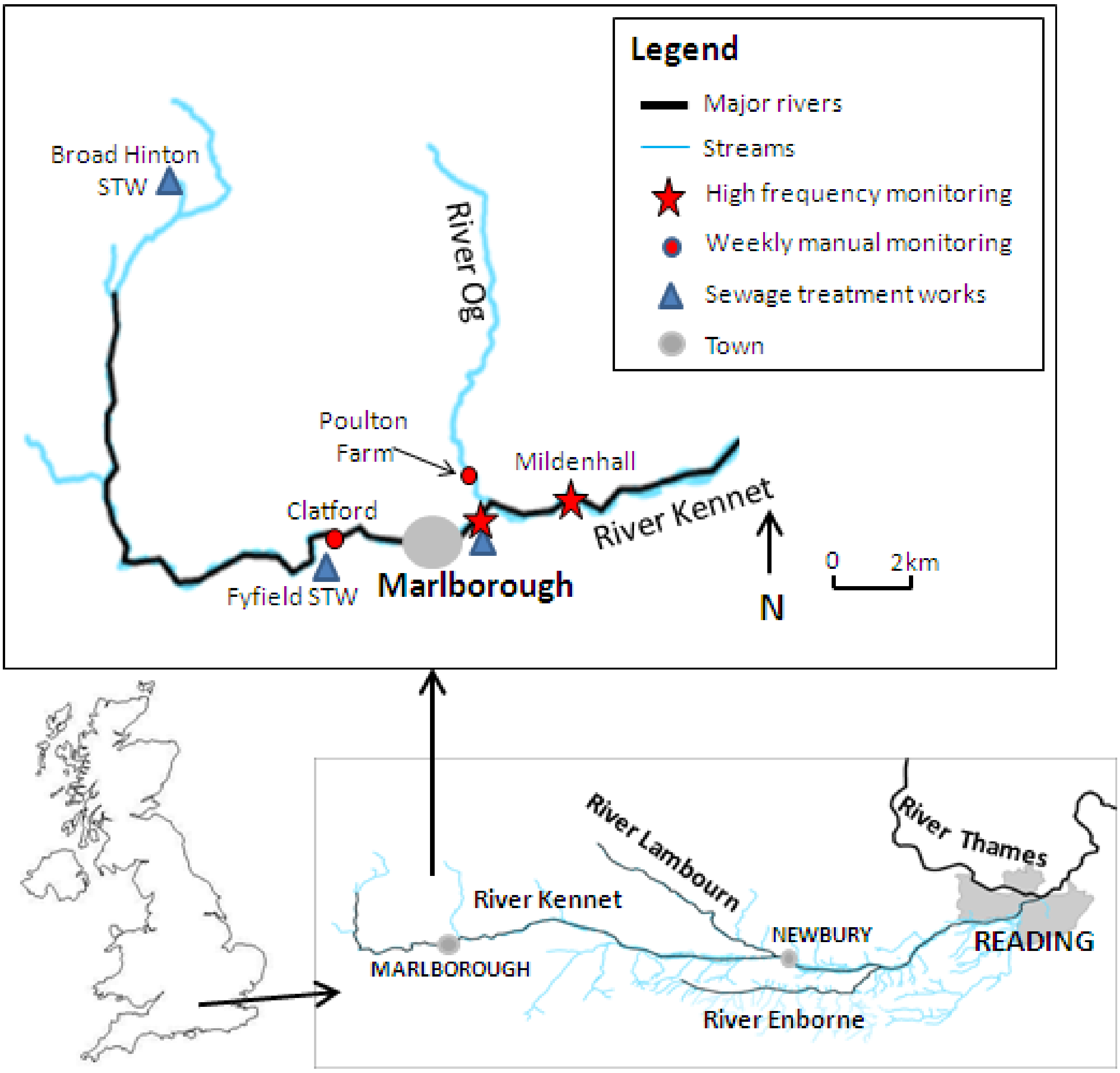

Figure 1. Map of the upper River Kennet catchment, showing locations of sampling sites.

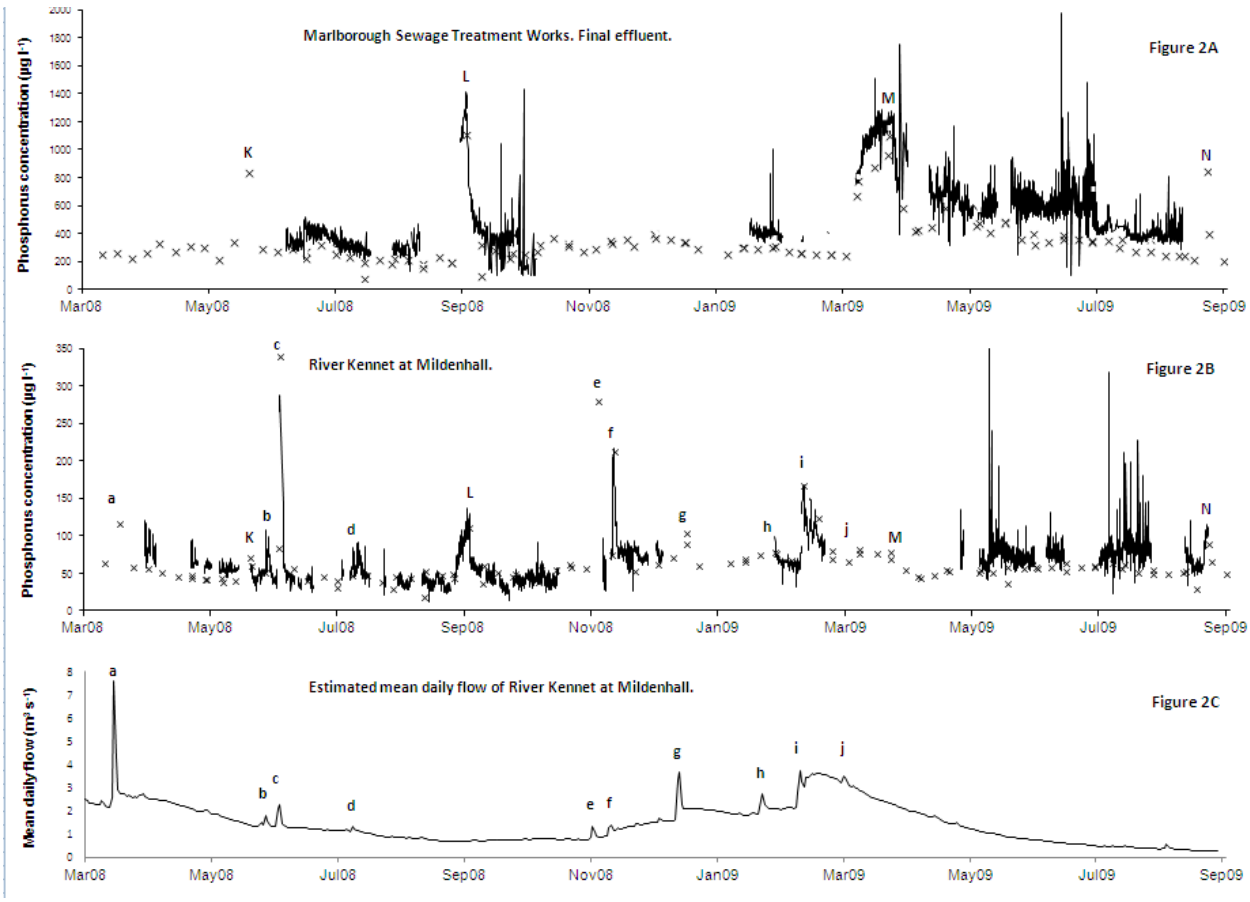

Figure 2. Timeseries of phosphorus concentrations of (A) Marlborough sewage treatment works final effluent and (B) the River Kennet at Mildenhall. The lines represent high frequency total reactive phosphorus concentrations from the Systea auto-analysers. The x symbols represent soluble reactive phosphorus concentrations from the manual sampling programme. The estimated volumetric flow of the River Kennet at Mildenhall is given in Figure 2C. Lower case letters (a-j) represent storm events. Upper case letters (K-N) represent periods of increased P concentration from Marlborough STW. (The high resolution TRP data is relatively unprocessed, with only the 'single point' peaks removed, and therefore many of the sporadic, short-duration peaks observed particularly in May to July 2009 will be attributable to instrument noise).

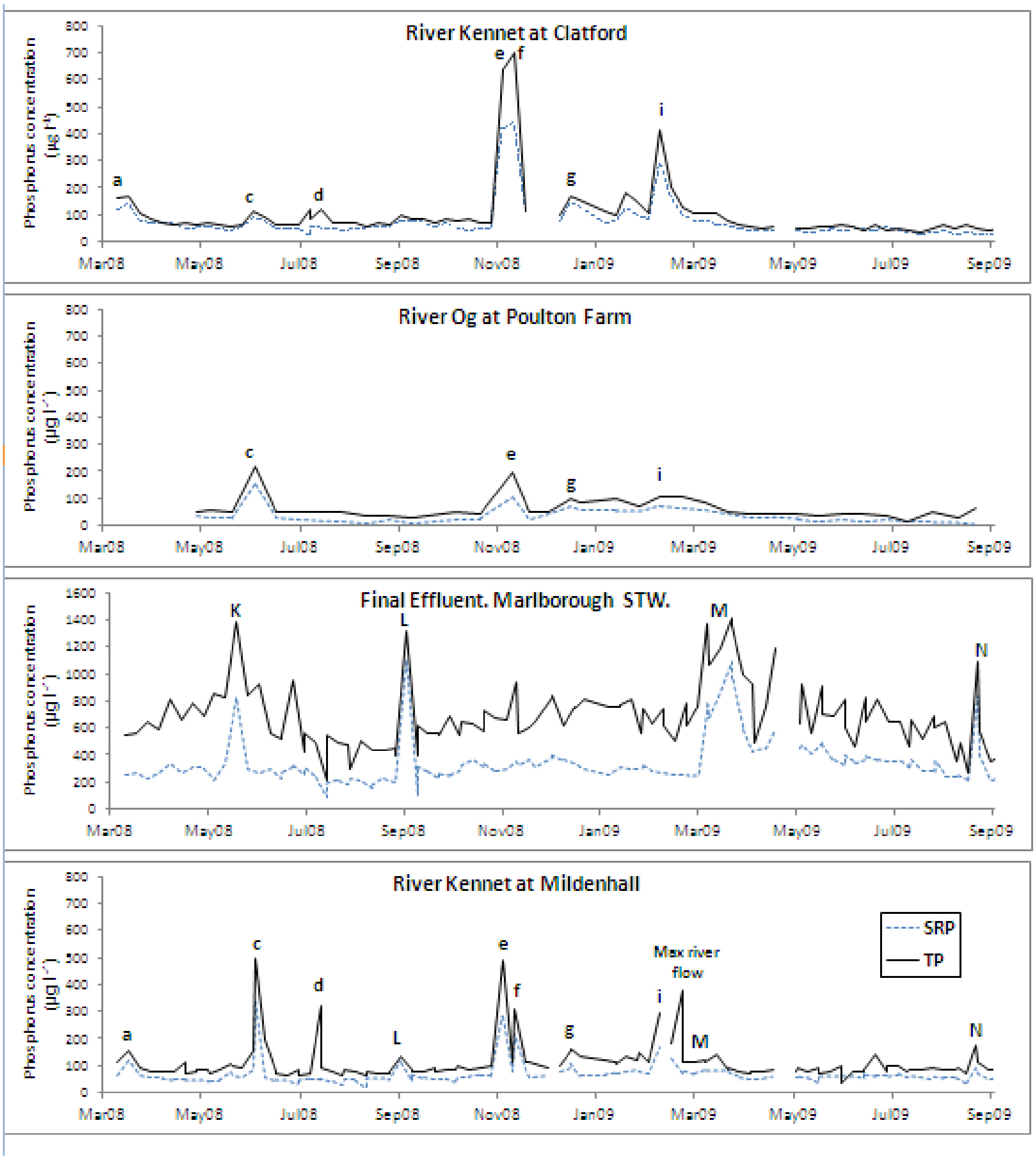

Figure 3. Total phosphorus and soluble reactive phosphorus concentrations for the River Kennet at Clatford, the River Og at Poulton Farm, Marlborough sewage treatment works final effluent and the River Kennet at Mildenhall. The lower case letters (a-j) represent the storm events (identified in Figure 2C). Upper case letters (K-N) represent periods of increased P concentration from Marlborough STW.

References

1. J. Hilton, M. O'Hare, M. J. Bowes and J. I. Jones, *Sci. Total Environ.*, 2006, **365**, 66-83.
2. S. R. Carpenter, N. F. Caraco, D. L. Correll, R. W. Howarth, A. N. Sharpley and V. H. Smith, *Ecol. Appl.*, 1998, **8**, 559-568.
3. V. H. Smith, G. D. Tilman and J. C. Nekola, *Environ. Pollut.*, 1999, **100**, 179-196.
4. R. H. Foy, *Soil Use Manage.*, 2007, **23**, 195-204.
5. A. C. Edwards and P. J. A. Withers, *Soil Use Manage.*, 2007, **23**, 133-143.
6. B. Kronvang, N. Vagstad, H. Behrendt, J. Bogestrand and S. E. Larsen, *Soil Use Manage.*, 2007, **23**, 104-116.
7. M. J. Bowes, C. Neal, H. P. Jarvie, J. T. Smith and H. N. Davies, *Sci. Total Environ.*, 2010, **408**, 4239-4250.
8. M. J. Bowes, J. T. Smith, H. P. Jarvie and C. Neal, *Sci. Total Environ.*, 2008, **395**, 125-138.
9. S. Greene, D. Taylor, Y. R. McElarney, R. H. Foy and P. Jordan, *Sci. Total Environ.*, 2011, **409**, 2211-2221.
10. H. P. Jarvie, P. J. A. Withers, M. J. Bowes, E. J. Palmer-Felgate, D. M. Harper, K. Wasiak, P. Wasiak, R. A. Hodgkinson, A. Bates, C. Stoate, M. Neal, H. D. Wickham, S. A. Harman and L. K. Armstrong, *Agric. Ecosyst. Environ.*, 2010, **135**, 238-252.
11. S. Barth, *Water Research*, 1998, **32**, 685-690.
12. H. P. Jarvie, P. J. A. Withers, R. Hodgkinson, A. Bates, M. Neal, H. D. Wickham, S. A. Harman and L. Armstrong, *J. Hydrol.*, 2008, **350**, 166-186.
13. P. Johnes, B. Moss and G. Phillips, *Freshw. Biol.*, 1996, **36**, 451-473.
14. B. Crabtree, S. Kelly, H. Green, G. Squibbs and G. Mitchell, *Water Sci. Technol.*, 2009, **59**, 407-416.
15. M. J. Bowes, J. Hilton, G. P. Irons and D. D. Hornby, *Sci. Total Environ.*, 2005, **344**, 67-81.

16. P. Jordan, J. Arnscheidt, H. McGrogan and S. McCormick, *Hydrol. Earth Syst. Sci.*, 2005, **9**, 685-691.

17. P. J. A. Withers, B. Ulen, C. Stamm and M. Bechmann, *J. Plant Nutr. Soil Sci.-Z. Pflanzenernahr. Bodenkd.*, 2003, **166**, 459-468.

18. M. J. Bowes, J. T. Smith and C. Neal, *J. Hydrol.*, 2009, **378**, 82-96.

19. P. Jordan, A. Arnscheidt, H. McGrogan and S. McCormick, *Hydrol. Earth Syst. Sci.*, 2007, **11**, 372-381.

20. E. J. Palmer-Felgate, H. P. Jarvie, R. J. Williams, R. J. G. Mortimer, M. Loewenthal and C. Neal, *J. Hydrol.*, 2008, **351**, 87-97.

21. A. Wade, E. J. Palmer-Felgate, S. J. Halliday, R. Skeffington, M. Loewenthal, H. P. Jarvie, M. J. Bowes, G. M. Greenway, S. J. Haswell, I. M. Bell, E. Joly, A. Fallatah, C. Neal, R. J. Williams, E. Gozzard and J. R. Newman, *Hydrol. Earth Syst. Sci.*, in press.

22. J. F. Wright, R. J. M. Gunn, J. M. Winder, R. Wiggers, K. Vowles, R. T. Clarke and I. Harris, *Sci. Total Environ.*, 2002, **282**, 121-142.

23. N. J. Flynn, D. L. Snook, A. J. Wade and H. P. Jarvie, *Sci. Total Environ.*, 2002, **282**, 143-157.

24. H. P. Jarvie, C. Neal, R. J. Williams, M. Neal, H. D. Wickham, L. K. Hill, A. J. Wade, A. Warwick and J. White, *Sci. Total Environ.*, 2002, **282**, 175-203.

25. C. Neal, E. Martin, M. Neal, J. Hallett, H. D. Wickham, S. A. Harman, L. K. Armstrong, M. J. Bowes, A. J. Wade and D. Keay, *Sci Total Environ*, 2010, **408**, 5306-5316.

26. H. P. Jarvie, C. Neal and R. J. Williams, *Water Air and Soil Pollution: Focus.*, 2004, **4**, 641-655.

27. C. Neal, H. P. Jarvie, A. Love, M. Neal, H. Wickham and S. Harman, *J. Hydrol.*, 2008, **350**, 154-165.

28. T. J. Marsh and J. Hannaford, *UK Hydrometric Register. Hydrological data UK series.*, Centre for Ecology and Hydrology, 2008.

29. A. J. Wade, P. G. Whitehead, G. Hornberger, H. P. Jarvie and N. Flynn, *Sci. Total Environ.*, 2002, **282**, 395-415.

30. J. Murphy and J. P. Riley, *Analytica chemica acta*, 1962, **12**, 31-36.

31. S. J. Eisenreich, R. T. Bannerman and D. E. Armstrong, *Environmental Letters*, 1975, **9**, 45-53.

32. C. Neal, M. Neal and H. Wickham, *Sci. Total Environ.*, 2000, **251**, 511-522.

33. H. K. G. R. Millier and P. S. Hooda, *J. Environ. Manage.*, 2011, **92**, 1210-1214.

34. H. P. Jarvie, C. Neal and P. J. A. Withers, *Sci. Total Environ.*, 2006, **360**, 246-253.

35. UKTAG., *UK Environmental Standards and Conditions (Phase 1)*, Technical Advisory Group on the Water Framework Directive, 2008.

36. C. Neal, M. Bowes, H. P. Jarvie, P. Scholefield, G. Leeks, M. Neal, P. Rowland, H. Wickham, S. Harman, L. Armstrong, D. Sleep, A. Lawlor and C. E. Davies, *Hydrol. Process.*, 2012, **26**, 949-960.

37. W. F. McDiffett, A. W. Beidler, T. F. Dominick and K. D. McCrea, *Hydrobiologia*, 1989, **179**, 97-102.

38. M. J. Bowes, W. A. House, R. A. Hodgkinson and D. V. Leach, *Water Research*, 2005, **39**, 751-762.

39. M. J. Bowes and W. A. House, *Hydrol. Process.*, 2001, **15**, 261-280.

40. J. W. Kirchner, X. H. Feng and C. Neal, *J. Hydrol.*, 2001, **254**, 82-101.

41. M. J. Bowes, K. Lehmann, H. P. Jarvie and A. C. Singer, in *British Hydrological Society International Conference*, University of Newcastle-upon-Tyne, Editon edn., 2010, p. 6.

42. M. J. Bowes, E. Gozzard, A. C. Johnson, P. M. Scarlett, C. Roberts, D. S. Read, L. K. Armstrong, S. A. Harman and H. D. Wickham, *Sci. Total Environ.*, 2012, **426**, 45-55.

43. M. J. Bowes, N. L. Ings, S. J. McCall, A. Warwick, C. Barrett, H. D. Wickham, S. A. Harman, L. K. Armstrong, P. M. Scarlett, C. Roberts, K. Lehmann and A. C. Singer, *Sci. Total Environ.*, 2012.

44. M. G. Hutchins, A. C. Johnson, A. Deflandre-Vlandas, S. Comber, P. Posen and D. Boorman, *Sci. Total Environ.*, 2010, **408**, 5065-5077.