Research article

The distribution of phosphorus in sediment and water downstream from a sewage treatment works

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In order to ensure the good ecological status of a range of waterbodies, as set out in the EU Water Framework Directive, a clearer understanding of nutrient sources and delivery mechanisms is required. Therefore, this study aimed to investigate the quantity and distribution of phosphates in Cam Brook, downstream from Paulton sewage treatment works (STW). Nine sites along a 2.6 km stretch of the river were surveyed; including one upstream of the STW, in October 2008 and the following February to determine whether there is seasonal variation in phosphorus concentrations. Water samples taken from each site were analysed for orthophosphate although sediment samples were analysed for orthophosphate and total phosphate. In February, water samples were further analysed for total phosphorus. Other variables such as dissolved oxygen (DO), water velocity, substrate, width, depth and land use were also surveyed to determine whether they influence the distribution of phosphorus. The water orthophosphate concentrations in Cam Brook significantly increased downstream from the STW in both October and February, rising from mean concentrations of 0.07–0.23 mg l^{-1}. This suggests that the STW was the major contributor to water orthophosphate concentrations. There was also strong negative correlation between water orthophosphate and DO concentrations in October (r-value −0.414) which could be due to the high biological oxygen demand of decomposers in the Autumn. There were large concentrations of total phosphate in the sediment which can be attributed to the small particle size of the substrate (clay) which increases its adsorption capacity. There were no seasonal variations in the water orthophosphate or sediment total phosphate concentrations although sediment orthophosphate concentrations were significantly higher in February (p-value < 0.001). However, orthophosphate still only accounted for a small proportion, at 3.47%, of the total phosphate concentrations in the sediment. The orthophosphate entering Cam Brook from the STW appears to be subject to a complex set of storage and transformation mechanisms which results in its storage as the non-bioavailable fraction of the total phosphate. Further research needs to be undertaken to determine the phosphorus cycling mechanisms that cause seasonal variation in sediment orthophosphate concentrations.

Key words: orthophosphate, total phosphate, phosphorus cycling, sediment, sewage treatment works, river.

Introduction

A number of external variables such as nutrients, season and flow regime influence the structure and function of aquatic ecosystems.[1] However, urbanization and agricultural intensification have caused phosphorus in particular, to switch from being the limiting nutrient for plant growth in many freshwaters,[2] to being present in excessive amounts causing 'stress' to aquatic ecosystems through eutrophication.[3] The sum of all phosphorus components in natural waters, total phosphorus (TP), is made up of phosphorus in particulate and soluble forms. Particulate phosphorus (PP) is a combination of organic and inorganic filtrate (>0.45 μm), although soluble phosphorus is made up of soluble unreactive phosphorus and soluble reactive phosphorus (SRP). The latter responds to colorimetric tests (molybdate reactive), is usually considered as bioavailable and is also known as dissolved reactive phosphorus or orthophosphate (H_3O_4P; as it is referred to hereafter).[4,5]

When phosphorus enters a channel, it undergoes various transformations due to the diverse range of physical, chemical and biological processes operating within river systems.[3]

Collectively termed phosphorus cycling, these processes involve the uptake and release of phosphorus by sediments and the conversion of phosphorus between organic, inorganic, particulate and dissolved forms.[6] The majority of PP entering a channel is simply deposited and stored as bed sediment whereas soluble phosphorus can be transferred via direct adsorption and desorption.[7] Where phosphorus is associated with calcium, below sewage treatment works (STW) or in calcareous rivers, it is likely to be transferred between the water column and sediment via precipitation and dissolution. In sewage/point-source dominated rivers where H_3O_4P concentrations in the water column are high, there is often a large concentration gradient which results in net uptake by sediments.[2] This observation highlights the 'self cleansing' capacity of rivers that can potentially reduce water phosphorus concentrations thus limiting plant growth.[8]

Anthropogenic sources of phosphorus entering rivers include point and diffuse inputs. Point sources include sewage and industrial effluent which frequently contain bioavailable H_3O_4P,[9] although diffuse phosphorus is predominantly of agricultural origin but also includes urban runoff.[10] Small amounts of naturally sourced phosphorus from atmospheric deposition, weathering, decomposition and bank erosion also enter rivers.[3] Research by Cooper et al.[11] suggests that 45% of phosphorus entering surface waters is of domestic origin and is usually discharged via STW, 45% is of agricultural origin and the remainder is from background sources. Jarvie et al.[12] studied 54 UK rivers to compare phosphorus inputs from point and diffuse sources. They found that even in agricultural catchments, point sources present a relatively greater risk of eutrophication as the continuously discharged effluent contains higher proportions of soluble phosphorus which is immediately available to algae and bacteria in the ecologically sensitive growing period when the dilution effect is at its lowest.[13] However, the adverse impacts of diffuse inputs are underestimated in the literature as although they are generally flushed into rivers in the form of unreactive particulate phosphorus during high flow conditions, they are deposited and stored in the bed sediments from which phosphorus can be utilized in ecologically sensitive periods.[6]

The distribution of phosphorus is also subject to seasonal variation whereby point-source dominated rivers have higher concentrations of bioavailable phosphorus in the summer as STW provide a constant source which is less dilute in the summer low-flow months.[13] House and Denison[14] observed accumulation of phosphorus during spring and summer low flows in the R. Wey and remobilization in autumn and winter storms as a result of scouring of bed sediments. Bowes et al.[15] further highlighted the importance of plant decomposition in the release of phosphorus in the autumn following bio-assimilation in the summer months. On the contrary, diffuse-source phosphorus dominated rivers exhibit higher water phosphorus concentrations following winter storm events when flows are increased. The river Frome, Dorset, displayed net retention of phosphorus to the river channel in the summer months due to bioaccumulation in biota and adsorption of phosphorus to bed sediments.[16] Decomposition of channel biomass, remobilization of bed sediments and increased diffuse inputs during storm events caused net generation in the autumn to spring months.

A huge amount of research has been undertaken to determine the effects of nutrients, predominantly phosphorus and nitrogen, on water quality. Any increase in phosphorus concentrations above those naturally present can increase macrophyte and algal growth, enhance microbial breakdown of biomass and cause distinct diurnal fluctuations in dissolved oxygen (DO) concentrations which ultimately lead to the mortality of anoxic-sensitive species.[17,18] Such eutrophication is one of the most serious problems associated with UK freshwater and is defined as the enrichment of environmental waters by anthropogenically sourced nutrients which often have adverse ecological and water resource impacts.

Maintaining good freshwater quality in the UK is vital in order to sustain aquatic resources, rural economies and amenity values,[19] hence the EC Urban Waste Water Treatment Directive (EU UWWTD) requirement to remove nutrients from all large STW (population >10 000).[20] This was followed by the new EU Water Framework Directive (WFD); Directive 2000/60/EC, which requires widespread control of nutrient inputs to rivers in order to achieve good ecological status of freshwaters by 2015.[21] Although there are no water quality standards for phosphorus set out in such Directives, a mean of $<100 \mu g \, P \, l^{-1}$ of H_3O_4P in river waters has been proposed in order to reduce the likelihood of eutrophication.[12] However, a study into phosphorus enrichment in 98 rivers in England and Wales revealed that 80% of the rivers failed to meet this target.[22] According to Neal et al.,[23] in order to increase the number of rivers meeting the WFD targets, more stringent effluent targets are needed ($>800 \mu g \, RP \, l^{-1}$). However, Bowes et al.[16] argue that due to already high nutrient loadings in UK rivers, phosphorus levels are not likely to decrease based on this alone, therefore further management techniques need to be considered.

In order to achieve the EU WFD objective to gain good ecological status of surface waters, biological and chemical phosphorus stripping has been implemented at large STW (population >10 000) in north-western Europe.[9] Biological treatment is environmentally sound as it does not produce any harmful by-products whereas chemical precipitation is much more efficient; lowering phosphorus levels to below $2 \, mg \, l^{-1}$, but has the added consideration of increased sludge production and the consumption/disposal of metal ions.[24] Biological P-stripping implemented at Marlborough STW in the upper Kennet has reduced levels of phosphorus

downstream from the point discharge to match upstream quantities.[9] However, further monitoring revealed that SRP concentrations were highly variable reflecting the variable efficiency of the biological phosphorus recovery process.[23] Nevertheless, biological phosphorus stripping and recycling for agro-industrial purposes has vast economic benefits for the water industry alongside the regulatory and ecological benefit of diverting 45 000 tonnes of phosphorus from river systems.[23–25] However, current UK efforts focus on minimizing diffuse-source phosphorus losses to rivers via catchment sensitive farming.[12]

Project aims

Eutrophication of freshwaters as a result of elevated phosphorus concentrations is becoming increasingly problematic in the UK. In order to improve the biological quality of these sensitive systems in a sustainable and cost-effective way, more in-depth understanding of the sources, transport and fate of phosphorus in rivers is required.[26] Previous studies have focused on phosphorus in the water column, however, this is only a small component of nutrient enrichment and future attention needs to be focused on phosphorus in bed sediments.[24] Therefore, this study aims to determine the quantity and distribution of phosphorus in water and sediments downstream from a STW and determine the variables that control phosphorus cycling between the two media. This work was carried out on the stretch of Cam Brook, a tributary on the River Avon, immediately downstream from Paulton STW.

Materials and methods

Survey area

A 2.6 km stretch of Cam Brook; a tributary of the River Avon, was studied from immediately above Paulton STW, Paulton, downstream to Radford Mill Farm, Radford (Fig. 1). This predominantly agricultural catchment is underlain by Keuper Marl, a Triassic clay, which is covered by a layer of alluvium along the river course.[27] Paulton STW (OS Grid Ref: ST 655575) serves ∼10 000 people and has the ability to treat flows received up to $72.3 \, l \, s^{-1}$.[28] The treatment process comprises of primary settlement (solids removal), biological treatment via trickling filters and further solid removal via secondary settlement but no tertiary treatment to remove nutrients.[28] In 2008, Paulton STW produced a total annual flow of 1 040 790 m^3 of fully treated effluent which was discharged into Cam Brook.[28]

Field work methodology

Nine sampling sites (Fig. 1) were selected along the river, of these, eight were downstream and one was upstream of Paulton STW. Further upstream sampling could not be carried out due to restricted public access and accessibility. A GPS was used to gain site co-ordinates which were then transferred onto a map of the catchment (Fig. 1). All nine sites were surveyed on 11th–12th October 2008 and again on 14th–15th February 2009 to determine seasonal variations in phosphate distribution. In order to prevent disturbed bed sediments flowing downstream and affecting other site results, sites were sampled by working upstream. February sampling was carried out following heavy precipitation thus high flows restricted data collection from sites C and E.

Six water samples were taken at each sampling site using an extendable sampling device in order to avoid disturbance of bed sediments. Water samples were also taken from the sewage outlet and two sources at site C; an agricultural drainage pipe and water running from an adjacent wetland. The width of the water column and the depth at six equidistant points across the width of the river were recorded. Velocity $(m \, s^{-1})$ and DO $(mg \, l^{-1})$ were also determined at six equidistance locations across the river using a basic flow metre and an Oxyguard Handy Mac III probe, respectively.

Figure 1. Ordnance survey map of Cam Brook including individual site locations; marked by a red square and the sewage treatment works outlet indicated with a red star.[42] © Crown Copyright/database right 2009. An Ordnance Survey/EDINA supplied service.

The DO probe was also used to determine the water temperature (°C) from the centre of the water column. Finally, six sediment samples were retrieved from each sampling site for analysis.

Laboratory analysis

A calibrated Griffin pH metre was immersed in the water samples for 30 s before the pH was recorded. As all water samples had a pH below 8, the blue method outlined by MAFF[29] was used to test for H_3O_4P. Wessex Water further analysed water samples collected in February for TP via inductively coupled plasma atomic emission spectroscopy. Sediment samples were air-dried, disaggregated and passed through a 2 mm nylon sieve before 20 ml of each sample and 50 ml of distilled water were shaken for 15 min. A calibrated pH metre was then immersed in the solution for 30 s before pH was recorded. The solution was filtered through Whatman No. 2 filter paper before being analysed for H_3O_4P using the same standard procedure carried out on the water samples.[29] Water-extractable H_3O_4P concentrations in sediment were expressed on a dry mass basis ($mg\,kg^{-1}$), assuming a porosity of 0.8 and a density of dry solids of $2400\,kg\,m^{-3}$.[30] The mass of H_3O_4P extracted was calculated by multiplying the concentration in the extract by the volume used for extraction (50 ml). This was then divided by the mass of dry solids extracted ($\sim$9.6 g). Sediments were further analysed for total extractable phosphate using one of two methods; Morgan's solution extraction method outlined by MAFF[29] was carried out on samples with a pH below 7.4 although the sodium bicarbonate extraction (Olsen's method) was used to analyse samples with a pH of 7.4 or above.[31]

Data analysis

Data analysis was carried out using Minitab version 15.0 and Microsoft Excel 2007 and data were presented in tables and graphs. Statistical significance was determined using two-sample T-tests, Mann–Whitney tests, two-way analysis of variance (ANOVA) and one-way ANOVA with Tukey's pair wise comparisons. Significant relationships between variables were also determined using Spearman's rank-order correlation analysis.

Results

Seasonal variations in site characteristics

The land surrounding Cam Brook is predominantly recreational grassland and the sampling area is tree-lined; the predominant species being Alder *Alnus glutinosa*. There was seasonal variation in the riverine substrate whereby site A–C were predominantly silt with boulders, cobbles and granules being more frequent downstream in October and a larger build up of silt throughout in February.

ANOVA indicates that the water depth was significantly higher (*p*-value < 0.001) in February than October at all sites except F, G and H, and that there was significant variation in water depth along the river in each month (*p*-value < 0.001). A two-sample T-test indicates that there was no significant difference in the width of the water column between October and February and no relationship was found between width and depth. There was a clear relationship between the water velocity in October and February where it rose and fell, respectively (Fig. 2) remaining consistently significantly higher in February (two-way
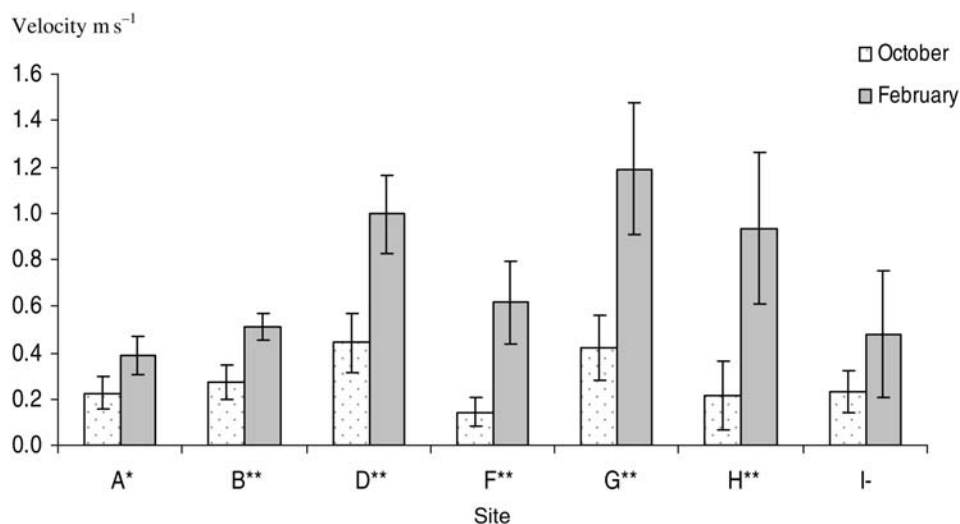
Figure 2. Seasonal comparison of the mean water velocity at each site including confidence intervals. *Note*: Sites C and E have been omitted as no data set exists for February. *Key*: -, not significant; *, significant; **, very significant; one-way ANOVA with Tukey's pairwise comparison for each individual site.

ANOVA p-value < 0.001). DO concentrations in Cam Brook were consistently higher in February. A two-way ANOVA confirmed that the overall seasonal difference was highly significant (p-value < 0.001) and there was also a significant difference in the DO concentrations between sites (p-value < 0.001) which was most likely due to site G, which had considerably lower DO levels in October. However, this is not typical of the site as this trend was not repeated in February.

Water samples

Cam Brook had a median water pH of 7.75 in October and 7.74 in February thus there was no significant difference in pH between the 2 months. Figure 3 shows variation in the H_3O_4P concentrations along Cam Brook where site A, before the sewage outlet, had significantly lower H_3O_4P concentrations than other sites in both months (p-value < 0.001). However, the water H_3O_4P concentrations at site I in October were also significantly lower than all other sites. Although the water H_3O_4P concentrations followed no obvious pattern in both months (Fig. 3), the concentrations were similar and a two-way ANOVA indicated that there was no significant seasonal variation.

In order to determine whether there was correlation between water H_3O_4P and DO concentrations in October, an anomaly (sample C1) was removed as this was most likely different from the other DO readings due to an outlet that was discharging water into that area of the river. An r-value of -0.414 indicated significant (p-value < 0.05) negative correlation between DO and water H_3O_4P in October, although there was no significant correlation in February. In February, water samples were further analysed for TP which displayed a relationship with

H_3O_4P whereby their concentrations were both low at site A and peaked at site C before steadily decreasing downstream (Fig. 4).

A sample was taken from the sewage outlet in October and with four being taken throughout the day in February. The H_3O_4P concentration in the sewage effluent was lower in February than October, but at 2.341 mg l^{-1} it was still considerably higher than the mean river water sample concentrations of around 0.2 mg l^{-1}. The water samples taken from wetland runoff and an agricultural drainage pipe at site C had a neutral pH and very low mean H_3O_4P concentrations at 0.037 and 0.063 mg l^{-1}, respectively.

Sediment samples

There was no significant difference between the sediment pH in October and February with median values of 7.60 and 7.64, respectively. There were, however, large site-specific variations in sediment H_3O_4P concentrations within each month highlighted by an overlap in confidence intervals at sites B, F, G and I (Fig. 5). There was no significant difference between October and February sediment H_3O_4P concentrations at these four sites; however, the overall seasonal difference was highly significant (p-value < 0.001).

There was a significant difference in the TP concentration between sites (p-value < 0.001) in October as concentrations oscillated down the river (Fig. 6). A one-way ANOVA with Tukey's pairwise comparison highlighted that site A, before the STW, had significantly lower TP concentrations in the sediment than all sites, except site F and H which also had low concentrations in October (Fig. 6). In February, the mean sediment TP concentrations displayed little variation along the river (Fig. 6) and although there was no significant difference, site A before the STW also
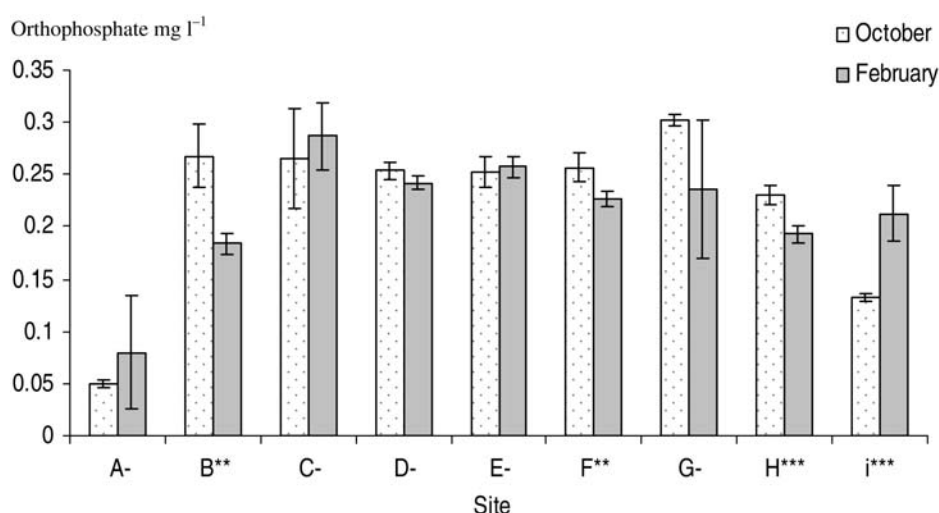

Figure 3. Seasonal comparison of the mean H_3O_4P (mg l^{-1}) concentration in the water samples taken from each site including confidence intervals. *Key*: -, not significant; **, very significant; ***, highly significant; one-way ANOVA with Tukey's pairwise comparison for each individual site.
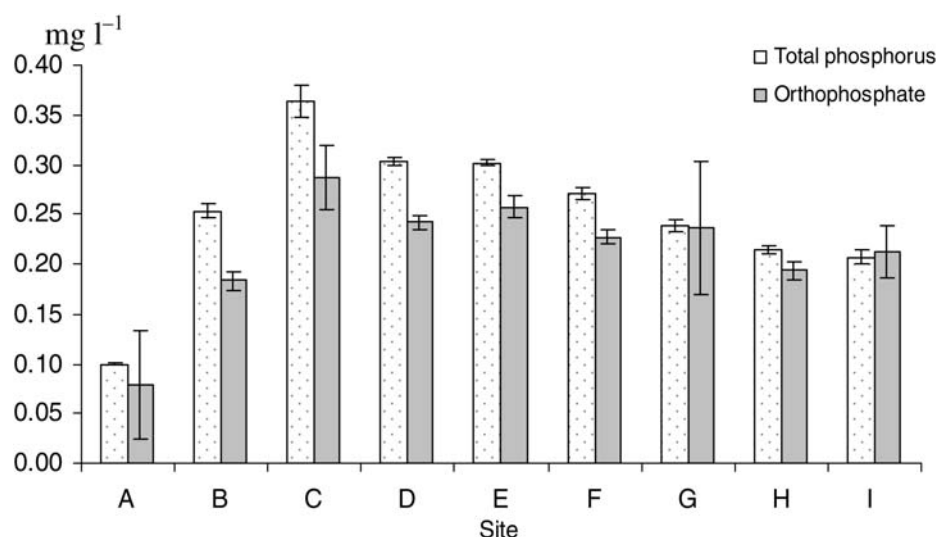
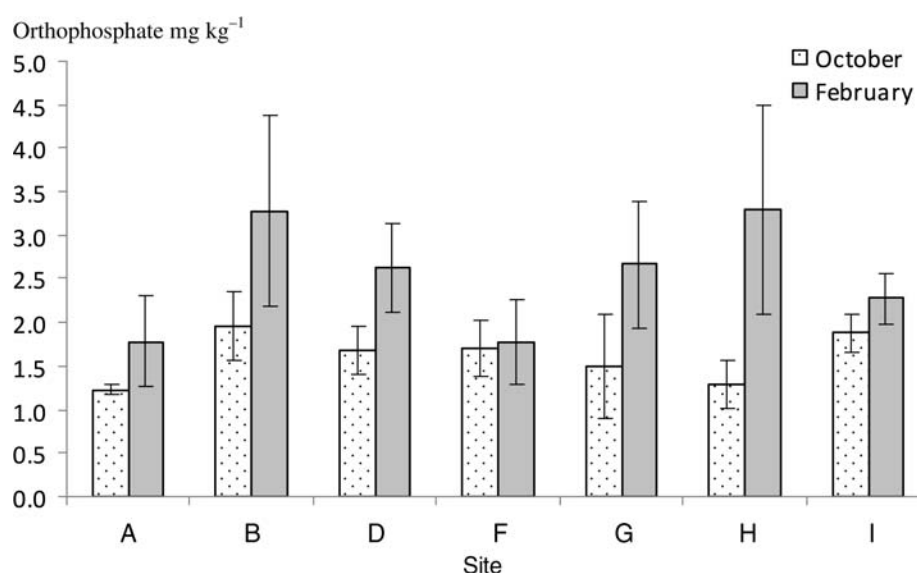**Figure 4.** The concentration of H_3O_4P and phosphorus in the water at each site in February including confidence intervals.

Figure 5. Seasonal comparison of the mean H_3O_4P concentration in the sediment at each site including confidence intervals. *Note*: Sites C and E have been omitted as no data were recorded for February.

had slightly lower TP concentrations compared with other sites. There was no significant difference between the October and February TP concentrations; however, different distribution patterns in the sediment downstream from the STW were observed in both months.

Phosphorus cycling

There was no significant correlation between water and sediment H_3O_4P in either October or February. There was

significant positive correlation between sediment H_3O_4P and TP concentrations in October (p-value < 0.001). However, in February there was no significant relationship between sediment H_3O_4P and TP concentrations (Fig. 7). There was significant positive correlation between water H_3O_4P and sediment total phosphate in October and February, with Spearman's rank-order correlation r-values of 0.399 (p-value < 0.05) and 0.340 (p-value < 0.05), respectively (Fig. 8).
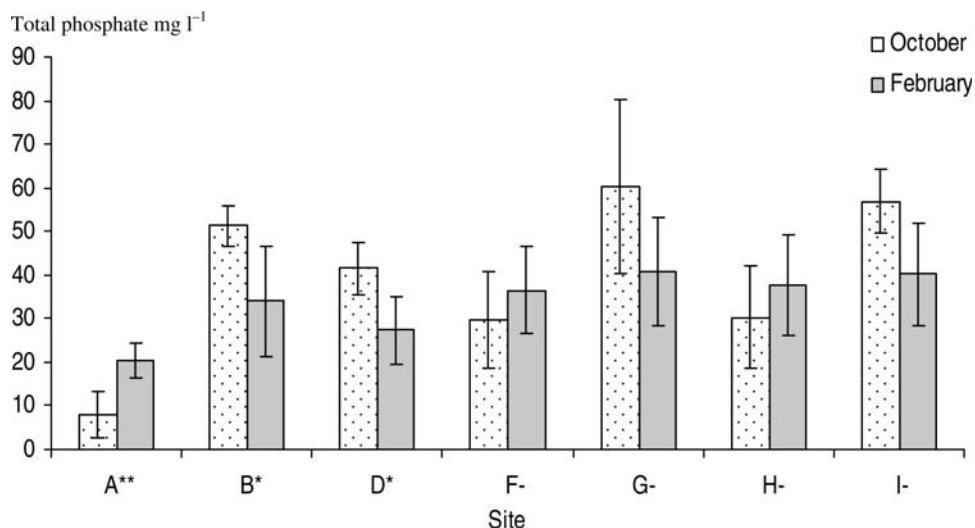
Figure 6. Seasonal comparison of the total phosphate concentration of the sediment at each site including confidence intervals. *Note*: Sites C and E have been omitted as no data were recorded for February. *Key*: -, not significant; *, significant; **, very significant; one-way ANOVA with Tukey's pairwise comparison for each individual site.
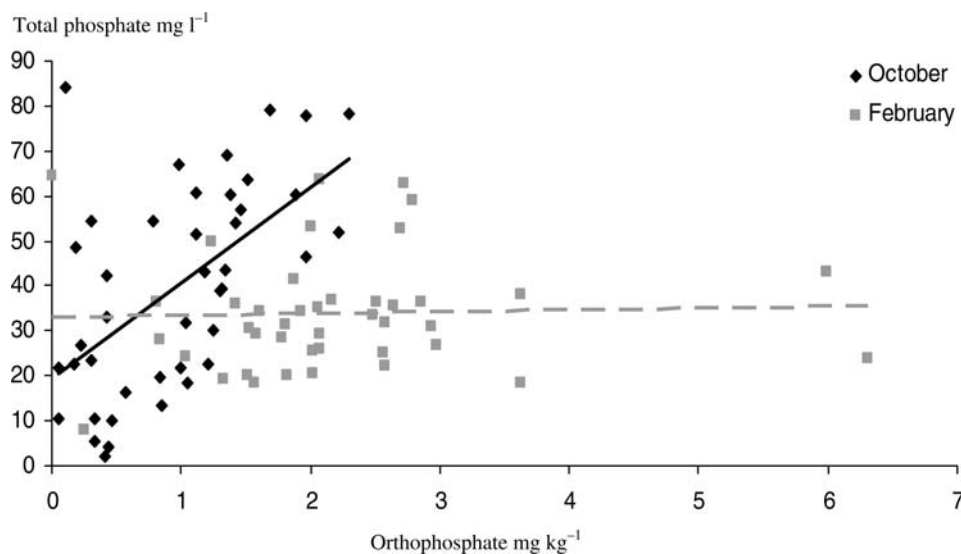

Figure 7. The relationship between sediment H_3O_4P and total phosphate concentrations in October and February. *Note*: Sites C and E have been omitted as no data set exists for February.

Discussion

Water samples

Mean H_3O_4P concentrations downstream from the sewage outlet in Cam Brook ranged from 0.11 to 0.30 mg l^{-1} (Fig. 3). This is similar to concentrations found in the R. Frome and the Enbourne at 0.14–0.35 and 0.15–0.23 mg l^{-1}, respectively.[13,32] Although H_3O_4P concentrations found in Cam Brook appear to be typical for the UK, phosphorus concentrations approaching 0.3 mg l^{-1}

greatly encourage the growth of macrophytes and algal communities.[24] Moreover, management targets to reinstate good ecological health in river systems recommend H_3O_4P concentrations between 0.002 and 0.1 mg l^{-1} (slightly higher in clay catchments such as Cam Brook).[24] This suggests that Cam Brook's H_3O_4P concentrations are higher than in rivers considered to be in good ecological health and further phosphate additions could lead to the river becoming eutrophic.

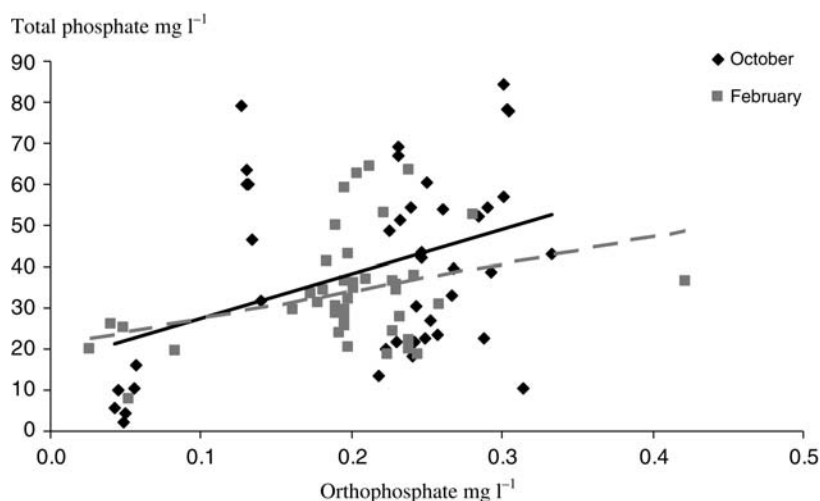The water H_3O_4P concentrations in Cam Brook were significantly lower upstream of the STW than downstream in

Figure 8. The relationship between water H_3O_4P and sediment total phosphate in October and February. *Note*: Sites C and E have been omitted as no data set exists for February.

both October and February; rising from mean concentrations of 0.05 and 0.08 mg l^{-1} upstream to 0.25 and 0.21 mg l^{-1} (Fig. 3). Bowes *et al.*[16] found similar increases in TP concentrations in response to minor and major STW. In the R. Arrow, already elevated TP concentrations of 0.72 mg l^{-1}, rose to a mean of 2.52 mg l^{-1} 3 km downstream from a major STW. Furthermore, TP concentrations in the R. Itchen increased from 0.2 mg l^{-1} upstream to 1.42 mg l^{-1} 2 km downstream of a minor STW. Therefore, it can be inferred that Paulton STW is the predominant source of high H_3O_4P and TP concentrations in the studied section of Cam Brook.

Following the peak in H_3O_4P concentrations immediately downstream from Paulton STW; in February there is a gradual decline in H_3O_4P concentrations whereas in October this decline occurs suddenly after site G (Fig. 3). Similar spatial variations in H_3O_4P concentrations are apparent in the first 4 km downstream from a STW in the R. Pang and the Lower Humber Rivers and Jarvie *et al.*[33] attributed such increasing losses to in-stream processes removing H_3O_4P from the water column.[23] Furthermore, Neal *et al.*[9] suggests that H_3O_4P concentrations may decrease within a shorter distance downstream than TP, due to a net influx to biota, algal films and sediments. This is reflected in a reduction in H_3O_4P concentrations to 80% of the TP content within a short distance downstream from the STW in the R. Frome.[34] This suggests that although there is only a slight decline in H_3O_4P concentrations in Cam Brook, had a larger stretch of the river been surveyed, the effects of in-stream processing may have become more apparent.

There is no seasonal variation in the quantity of H_3O_4P in Cam Brook. However, literature suggests that if a river is point-source dominated, water H_3O_4P concentrations is often higher during low-flow periods when the dilution effect is at its lowest.[13,15,23,32] The lack of seasonal variation but high inter-season variation in Cam Brook's H_3O_4P concentrations suggests that either the STW is not the only source of phosphorus, or other in-stream processes may be becoming more influential during low-flow periods.[26] Bowes *et al.*[13] observed a cyclical annual pattern in H_3O_4P concentrations in the R. Frome where the lowest concentrations occurred in April and May and the highest in the low-flow periods between July and October. As Cam Brook was only sampled in the intermediate periods of October and February, further monthly research would be required to determine any significant seasonal variations in the quantity and distribution of phosphorus which are not apparent in this study.

There was negative correlation between DO and water H_3O_4P concentrations in Cam Brook in October. This could be attributed to the breakdown of organic matter occurring in the Autumn causing a decrease in DO due to elevated biological oxygen demand, and an increase in water H_3O_4P concentrations due to the release of phosphorus stored in plant tissues.[32] No correlation was found between DO and water H_3O_4P in February which could be due to other in-stream processes controlling H_3O_4P concentrations during high flows.

Water H_3O_4P and TP followed the same distribution pattern downstream from the STW (Fig. 4). Jarvie *et al.*[12] found similar results where H_3O_4P made up a large component of TP and the two variables were significantly correlated with an *r*-value of 0.88. The H_3O_4P concentrations in Cam Brook account for a mean of 85.8% of the TP concentration in the water column whereas H_3O_4P accounted for as little as 50% of the TP in the Lambourn and Enborne[32] and 77% in the R. Kennet.[23] This suggests that H_3O_4P constitutes varying proportions of TP in different rivers.

The sewage effluent discharged into Cam Brook in February contained 3.125 mg l^{-1} of TP, 74.9% of which was in the form of H$_3$O$_4$P. Cooper et al.[11] found higher proportions of H$_3$O$_4$P at 96% in sewage effluent discharged into the R. Thame. High concentrations of H$_3$O$_4$P such as these entering rivers often boost concentrations in river water to above 0.10 mg l^{-1} which can greatly increase the risk of eutrophication.[8] Bowes et al.[16] studied the R. Avon catchment and found that in 44 out of 45 incidences of total phosphate concentrations exceeding 5 mg l^{-1}, a STW contributed to over 66% of the TP load. This is also evident in Cam Brook as H$_3$O$_4$P concentrations remained below 0.10 mg l^{-1} at the upstream point and increased to a mean of 0.24 mg l^{-1} downstream from the STW. Although this indicates that effluent discharged from Paulton STW increases the H$_3$O$_4$P concentrations in Cam Brook, further upstream sampling would have provided a more robust data set from which to draw firm conclusions. There was also seasonal variation in H$_3$O$_4$P concentrations in sewage effluent discharged into Cam Brook at 3.67 mg l^{-1} in October and 2.34 mg l^{-1} in February which could be attributed to the dilution of sewage following high precipitation rates.

The amount of diffuse-source phosphorus entering rivers is dependent on rainfall, hydrological conditions and land use in the watershed.[35] The land surrounding Cam Brook is predominantly recreational grassland thus is unlikely to significantly increase H$_3$O$_4$P concentrations as the topsoils are largely unimproved.[36] The trees and vegetation lining Cam Brook may also act as a buffer strip by removing a large majority of nutrients from the soil before they reach the river system. Furthermore, H$_3$O$_4$P concentrations only account for 50% of TP in agricultural runoff at its highest, and concentrations in sewage effluent are at least one order of magnitude higher.[11,34] This corresponds to the low H$_3$O$_4$P concentrations found in the agricultural and wetland runoff into Cam Brook which is less than the average concentrations in the water column. However, runoff consists of a large proportion of unreactive particulate phosphorus (60–90%) which was not accounted for in this study and should not be underestimated as it can be subsequently released as H$_3$O$_4$P in the growing season.[6,37]

Sediment samples and phosphorus cycling

The sediment and water pH in Cam Brook remained slightly alkaline, at pH 7.6 and 7.7, which is indicative of the slightly calcareous Keuper Marl geology rather than biotic influences as no seasonal variations were evident. However, the sediment H$_3$O$_4$P concentrations in Cam Brook were significantly higher in February which could be due to net retention of phosphorus in sediment during high winter flows and subsequent release during summer low flows.[37] According to Meyer and Likens[38] seasonal variation in phosphorus retention is dependent on a number of interrelated factors such as temperature and biological activity. A controlled experiment by House et al.[5] suggests that a net influx of H$_3$O$_4$P to bed sediments occurs with increasing water velocity. This parallels data from Cam Brook whereby H$_3$O$_4$P concentrations remained higher in February when water velocity was highest.

In Cam Brook, the effluent-derived H$_3$O$_4$P is not directly contributing to the sediment H$_3$O$_4$P concentrations as they remain low and do not increase downstream from the STW. This is highlighted by the lack of correlation between H$_3$O$_4$P in the sediment and water in both October of February. Furthermore, as water H$_3$O$_4$P was correlated with sediment TP, it is likely that the water H$_3$O$_4$P in Cam Brook is not simply transferred to sediment but undergoes a complex set of transformation mechanisms which affect the fractionation of sediment phosphorus.[32] Sediment H$_3$O$_4$P concentrations were also considerably lower than total phosphate concentrations and accounted for as little as 1.58 and 3.47% in October and February, respectively. Thus the positive correlation between sediment H$_3$O$_4$P and total phosphate could be attributed to the H$_3$O$_4$P making up a certain fraction of the total phosphate.

Cam Brook exhibited high mean sediment TP concentrations of 39.79 mg l^{-1} in October and 33.89 mg l^{-1} in February (Fig. 6). This is indicative of Cam Brook's Keuper Marl clay ($<2\ \mu$m) geology which has a small substrate particle size and consequently larger particle surface area for increased phosphorus sorption.[3,24] However, caution is needed when drawing conclusions about the exact concentrations of TP as two different analytical methods were used, dependent upon sample pH. These methods have been shown to extract differing quantities of phosphorus.[30] Therefore, further research would benefit from using a single method that is relatively independent of pH, such as anion-exchange resin extraction.[39]

The TP concentrations in the sediment are considerably higher than the H$_3$O$_4$P concentrations found in the water column suggesting that geochemical processes are taking place causing phosphorus to be retained. This occurs in many streams and rivers receiving sewage effluent and is termed the 'phosphate buffering method'.[5,6,35,40] It allows relatively constant concentrations of phosphates to be maintained within a river as is occurring in Cam Brook.[41] Furthermore, the sediment TP concentrations were significantly lower upstream of the STW than downstream in both October and February. Therefore, the sediment in Cam Brook is buffering the impacts of the anthropogenic phosphorus inputs on downstream ecosystems, which is particularly important in the growing season when flows are generally lower.[3] As with sediment H$_3$O$_4$P, the distribution of TP (Fig. 6), related to water velocity whereby sites F and H with the lowest TP concentrations also had the lowest water velocity. No other variables considered in this study follow a similar pattern thus it appears that velocity is

influencing TP concentrations. However, further research would need to be conducted to determine the extent of the relationship between water velocity and sediment TP and to ascertain the influence of other variables not considered in this investigation.

Conclusion

It is clear that H_3O_4P concentrations in Cam Brook are considerably higher than those favoured by good ecological status; however, concentrations such as these are no longer uncommon in the UK. Diffuse-source phosphorus appeared to have an insignificant impact on water H_3O_4P concentrations whilst the STW is thought to be the main contributor to these raised H_3O_4P concentrations in both October and February as concentrations upstream remained within acceptable limits. Furthermore, H_3O_4P concentrations made up a large quantity of the TP in the water in February which is indicative of highly bioavailable sewage effluent rather than diffuse-source phosphorus which is predominantly in particulate form.

Cam Brook had high sediment total phosphate concentrations in both October and February as it lies in a clay catchment with high phosphorus adsorption capacity. However, H_3O_4P only made up a small fraction of sediment total phosphate concentrations. Therefore, as there was positive correlation between water H_3O_4P and sediment TP concentrations, water H_3O_4P is most likely undergoing complex transformation mechanisms which result in its storage as a non-bioavailable fraction. However, further research needs to be undertaken to determine the relative contribution of phosphorus cycling mechanisms which cause spatial and temporal variation in sediment phosphorus concentrations.

Acknowledgements

Author biography

Jo-Anne has just completed a BSc (Hons) Environmental Science course at Bath Spa University and is now continuing her studies with an MSc in Environmental Water Management at Cranfield University. On completion she would like to pursue her interests in aquatic ecosystems by undertaking further research.

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