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Understanding the controls on sediment-P interactions and dynamics along a non-tidal river system in a rural–urban catchment: The River Nene

A.M. Tye [a], [*], B.G. Rawlins [a], J.C. Rushton [a], R. Price [b]

[a] British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK
[b] Environment Agency, Nene House, Pytchley Lodge Industrial Estate, Kettering, NN15 6JQ, UK

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ABSTRACT

The release of Phosphorus (P) from river sediments has been identified as a contributing factor to waters failing the criteria for ‘Good Ecological Status’ under the EU Water Framework Directive (WFD). To identify the contribution of sediment-P to river systems, an understanding of the factors that influence its distribution within the entire non-tidal system is required. Thus the aims of this work were to examine the (i) total (P$_{Total}$) and labile (P$_{Labile}$) concentrations in sediment, (ii) the sequestration processes and (iii) the interactions between sediment P and the river water in the six non-tidal water bodies of the River Nene, U.K. Collection of sediments followed a long period of flooding and high stream flow. In each water body, five cores were extracted and homogenised for analysis with an additional core being taken and sampled by depth increments. Comparing the distribution of sediment particle size and P$_{Total}$ data with soil catchment geochemical survey data, large increases in P$_{Total}$ were identified in sediments from water body 4–6, where median concentrations of P$_{Total}$ in the sediment (3603 mg kg^{-1}) were up to double those of the catchment soils. A large proportion of this increase may be related to in-stream sorption of P, particularly from sewage treatment facilities where the catchment becomes more urbanised after water body 3. A linear correlation ($r = 0.8$) between soluble reactive phosphate (SRP) and Boron in the sampled river waters was found suggesting increased STW input in water bodies 4–6.

P$_{Labile}$ concentrations in homogenised cores were up to 100 mg kg^{-1} PO$_4$–P (generally < 2% of P$_{Total}$) and showed a general increase with distance from the headwaters. A general increase in Equilibrium Phosphate Concentrations (EPC$_0$) from an average of 0.9–~1.7 μm L^{-1} was found between water bodies 1–3 and 4–6. Fixation within oxalate extractable phases (Al, Fe and Mn) accounted for ~90% of P binding in water bodies 4–6, but only between 31 and 74% in water bodies 1–3. Statistical models predicting P$_{Total}$ ($R^2 = 0.78$), oxalate extractable P ($R^2 = 0.78$) and Olsen P ($R^2 = 0.73$) concentrations in river sediments identified Mn oxy-hydroxides (MnO$_x$) as a strong predictive variable along with the location within the river system. It is suggested that MnO$_x$ within model predictions is identifying a pool of mixed Fe–Mn oxy-hydroxides (MnO$_x$–FeOOH) or Fe oxy-hydroxide (FeOOH) from the wider Fe$_{Oxalate}$ pool that are particularly effective at sorbing and fixing P. The findings demonstrate how sediment and P may accumulate along a 100 km non-tidal river system, the extent to which a range of processes can fix P within mineral phases and how natural flooding processes may flush sediment from the river channel. The processes identified in this study are likely to be applicable to similar river systems over their non-tidal water bodies in eastern England.

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1. Introduction

A principal aim of the EU Water Framework Directive (Directive EC, 2000/60/EC) is to prevent further deterioration and to improve the quality of surface waters (rivers and lakes), groundwater and coastal waters and to promote ‘good ecological status’ (GES) with

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[*] Corresponding author.
E-mail address: atye@bgs.ac.uk (A.M. Tye).

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respect to biodiversity in rivers (Johnes et al., 2007; EA, 2014). Phosphate is the major nutrient in rivers that is typically in shortest supply, relative to the stoichiometric requirements of plants, and therefore has the greatest potential to limit river productivity (Mainstone and Parr, 2002). Thus, soluble reactive P (SRP) concentrations exceeding target concentrations (Mainstone, 2010) in river water is a common reason why GES is often not achieved. Major inputs of phosphate in river waters are from point sources such as sewage treatment plants (Jarvie et al., 2006; Neal et al., 2010) or diffuse sources such as agricultural land where phosphorus (P) enters the river channel primarily attached to soil particles (Bilotta et al., 2010; Quinton et al., 2010). Common pathways for agriculturally derived sediment bound P are either via soil erosion (Haygarth et al., 2006; Quinton et al., 2010) or through under field land drainage systems (Bilotta et al., 2008; Reid et al., 2012). In addition, dissolved P from field drains is increasingly recognised as a source (King et al., 2015). Detrimental outcomes for rivers include (i) shifts to more eutrophic communities, and (ii) potential future desorption of phosphate from the sediment to the water body (McDowell et al., 2003; Jarvie et al., 2005).

In-channel cycling of P involves a complex set of interactions between water, sediment and aquatic biota. It involves various species of P including soluble reactive phosphorus (SRP), particulate P (PP) and organic forms of phosphorus (Mainstone et al., 2000). Despite significant efforts by regulatory bodies, water companies and land managers to decrease SRP concentrations in river waters, these efforts have often failed to improve SRP concentrations to the desired extent. The problem of ‘legacy P’ (the P that has accumulated along the land-water continuum from past management practices) have been cited (Sharpley et al., 2013; Jarvie et al., 2013) with sediment P being identified as a potential source (House and Denison, 1997; Collins et al., 2007; Bilotta et al., 2010).

River sediment can act as both a sink and a source for SRP, depending on the prevailing geochemical conditions. These interactions are highly dependent on sediment architecture, water velocity, sediment and water chemistry (House and Warwick, 1999). Within a catchment, variation in geology and land-use will change (i) the geochemistry and mineralogy of the sediment and (ii) the amount of P entering the channel. Within the length of the river channel the hydromorphology, vegetation and water velocity will determine the size distribution of and residence time of the sediment (Naiman et al., 2000; Fisher et al., 2004; Heppell et al., 2009). In addition, redox status and the dissolution and re-precipitation of metal oxides are considered essential for the sorption and fixation of SRP (Reddy et al., 1995; House and Denison, 2000). The nature of the catchment geology will also determine river water chemistry which may influence in-channel mineral precipitation (e.g. Ca-apatite) contributing to the removal of SRP from the river system (House and Denison, 1997, 2002).

Three parameters interact to determine the role of sediment in controlling SRP concentrations in the water column; (i) the size of the labile pool of P (P_{Labile}) in the sediment, (ii) the equilibrium phosphate concentration (EPC_0) and (iii) the rate of fixation or release that P may undergo. Where P_{Total} includes all the inorganic and organic P species, the P_{Labile} pool represents that pool of P that is potentially able to respond to changes in the solid-solution equilibria. The concentration of P_{Labile} can increase rapidly through sorption with increases in SRP inputs as has been demonstrated downstream of sewage works (Jarvie et al., 2006). The most easily desorbable component of P_{Labile} is likely to buffer the solid ↔ solution equilibria through the EPC_0, which is defined as the solution concentration of SRP at which there is no net release or uptake of SRP by the sediment and is sometimes referred to as the instantaneous labile pool (Hartikainen et al., 2010). The instantaneous labile pool and EPC_0 are often related through Quantity/Intensity relations using either Langmuir or Freundlich isotherms (Hartikainen, 1991; Jarvie et al., 2005; Withers et al. 2009). After SRP is sorbed onto the sediment, it has the potential to move to the non-labile pool through fixation onto predominantly metal oxides, with the amorphous or non-crystalline pool of Fe, Al and Mn oxides considered important sorptive phases (Hartikainen et al., 2010).

This paper reports on changes in the sediment-P status in the six main Water Framework Directive (WFD) water bodies of the non-tidal River Nene (Tye et al., 2013). Within the River Nene, sediment and P are often interlinked with plant growth and the siltation of the river course. Therefore, to understand the contribution that sediment-P may make to SRP concentrations the spatial distribution and dynamics of sediment-P within the whole or substantial parts of the river system needs to be understood. Thus the aims of this work are (i) to examine the how P_{Total} varies in sediments and the degree to which the sediment has been enriched or depleted in P relative to catchment soils, (ii) to understand the processes through which P is fixed into non-labile pools with distance from the headwaters and (iii) to understand how P_{Labile} concentrations might effect SRP concentrations. Whilst previous studies have examined sediment P relationships in selected river locations in the UK, few studies have examined sediment P interactions along complete stretches of the non-tidal river systems (e.g. ~100 km). In particular, this paper focuses on the possible effects of the rural–urban catchment transition and how sediment geochemistry controls the interactions between sediment P and water.

2. Materials and methods

2.1. The Nene Catchment

The river Nene is the 10th longest river in the UK and rises in Northamptonshire, flowing in a north-easterly direction out to the sea via the town of Northampton and City of Peterborough (Fig. 1). It is 161 km long and has a total catchment area of 2270 km^2. The river is navigable from the sea as far as Northampton where it connects with the Grand Union Canal. It is a slow flowing river that has suffered from major siltation and macrophyte growth in the past. For example, in 1930 the River Nene Catchment Board was established to undertake extensive dredging and improve sediment management (Meadows, 2007).

The catchment for the upper six water bodies of interest in this study has an area of 1590 km^2 (Fig. 1). The floodplain is relatively wide (from a few hundred metres to ~2 km) and the channel frequently bifurcates and re-joins, as well as being heavily engineered in sections (Williams and Fawthrop, 1988; Meadows, 2007). The river course falls from ~160 m above ordnance datum (AOD) at source to ~6 m AOD at Peterborough. The majority of this fall occurs in the first 9.5 km, with the channel lying at 80 m AOD in water body 1 (Meadows, 2007). Whereas several urban centres are based on the Nene, particularly Northampton, the major land use is agriculture, mainly arable (cereals and oilseed rape) and grazing. Buffer strips are commonly present on arable land adjacent to the river. A major source of sediment input from arable land is via under field drainage which is extensive as the soils developed on the mudstone geology that dominates the catchment are slow draining. This was identified as a major source during sampling where drains were discharging straight into the river (A. Tye, *pers. comm.*) The concentration of 0.12 mg L^{-1} (3.87 μm L^{-1}) SRP is proposed for Good Ecological Status for the Nene (River Type 4n; Altitude >80 m; Alkalinity >50 mg L^{-1} $CaCO_3$) (Mainstone, 2010; UKTAG, 2012). Current concentrations of SRP in the Nene often

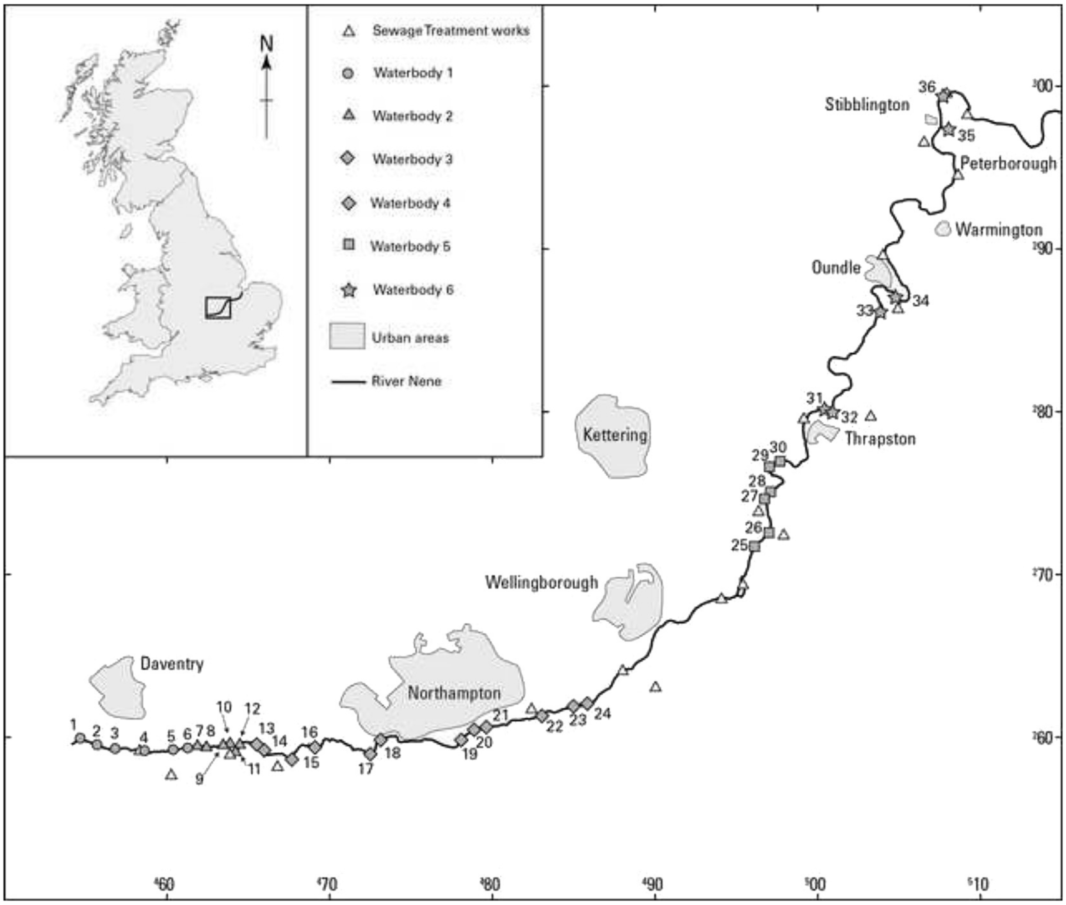

Fig. 1. Map of the sampling locations in each of the six water bodies of the River Nene referred to in this study. Six samples were taken from each of the six water bodies marked by different symbols (see key). Sewage Treatments works that discharge to the Nene are also shown. Coordinates show kilometres of the British National Grid.

exceed the WFD limits (Atkins, 2014).

2.2. Catchment geology

The bedrock geology and soil parent materials of the River Nene catchment comprises rocks of the Lias group and are predominately the Dyrham Formation (interbedded siltstones and mudstones) for water bodies 1–3, and the Whitby Mudstone formation (water bodies 4–6) (Cox et al., 1999). There is also a small area of Charnmouth mudstone within water bodies 1–3, but this is very much a minor component. The Nene Catchment is beyond the southern ice limit of the Devensian stadial but some glacial outwash is found in the catchment. These glaciogenic sediments are underlain by sands and gravels (Milton Sand) that represent earlier trunk rivers (Brown et al., 1994). Significant extraction of this sand and gravel has occurred along some reaches of the river, leaving a range of adjacent wetland environments. On the modern floodplains alluvial soils and deposits are found.

2.3. Sampling strategy and site selection

The River Nene was sampled from the source waters down to the west of Peterborough, this being the non-tidal section, and divided into six WFD water bodies by the Environment Agency (see Fig. 1). The sampling strategy was designed to obtain robust estimates of sediment P_{Total} and P_{Labile} concentrations in each of the six water bodies with a reasonable estimate of variability. Therefore five sediment cores were collected from each water body to be homogenised prior to analysis, whilst a sixth core ($Core_D$) was extracted from each water body to allow analysis of P_{Total} and P_{Labile} variations with depth. A desk-top study was undertaken to locate sampling sites. In the upper water bodies these were as regularly spaced as possible. For water bodies 4, 5 and 6 a boat was used for sampling, so positions were partially determined by the available boat launch sites and travelling distance upstream and downstream. Sampling was undertaken in the winter so little information regarding potential habitats of sediment sampled was available. Thus the sampling aimed just to take representative samples of sediment at each site. Fig. 1 shows the location of the cores extracted. The $Core_D$ samples were extracted from positions 2, 7, 15, 20, 28 and 35 (Fig. 1).

2.4. Collection of sediments

Sampling followed the very wet autumn/winter of 2012/13 in January and February 2013, a time of unusually long periods of flooding and high river flows. River flow was still above base-flow when the samples were collected. Cores were taken by pushing a length of polycarbonate tube (diameter = 58 mm internal diameter) into the sediment and retention was through the use of a core catcher, at the base of the tube. Due to the long period of flooding and high river flow (6–8 weeks) prior to sampling insufficient sediment was found at 9 sites in the upper 3 water bodies to collect a core sample. At these sites a sample of the sediment (predominantly sand and gravel) was taken from shallow water close to the edge of the river. The sample size collected from these sites was

>3 kg so that a representative sample could be obtained. All samples were kept <4 °C after sampling. A water sample was collected at each of the Core$_D$ sample sites to determine SRP and hydrochemistry. The water sample was filtered immediately after collection through a 0.45 μm syringe filter and kept in the dark at <4 °C until SRP analysis, within 5 days of collection (Jarvie et al., 2002). The total depth of sediment present at each sampling location was examined by probing at each site. Measurements of sediment depths were collected ($n = 10$) within a 20 m distance up and down from the sampling site.

2.5. Sediment sample characterisation

Due to the size and number of samples the five homogenised core samples taken from each water body were air-dried (<30 °C) before being sieved to <2 mm. The depth of core was recorded and the mass of air-dry sediment from each of these cores in each water body was weighed. The core designated for depth analysis within each water body (Core$_D$) was divided into 5 segments, with the top section always being 0–5 cm depth from the sediment surface, this being the standard depth on which EPC$_0$ and sorption/desorption kinetic analysis are undertaken (Jarvie et al., 2005). The top 0–5 cm was wet-sieved <2 mm and stored <4 °C. After measurements of EPC$_0$ and P uptake kinetics were undertaken, the remainder of these samples was air-dried for other analyses. The rest of Core$_D$ was divided into four equal sections and air-dried immediately, before being sieved to <2 mm.

Estimates of the quantity of organic matter in the sediment samples were undertaken by loss on ignition; 1 g of sample was ignited at 475 °C for 4 h. P$_{\mathrm{Total}}$ (all species of inorganic and organic P) analysis was undertaken using a UKAS accredited method based on Sulcek and Povandra (1992). Subsamples of the dried sediment (~30 g) were ground in an agate mill to <150 μm. Milled samples were digested by weighing 0.25 g of soil into a Savillex™ vial and adding HF, HNO_3 and $HClO_4$ concentrated and analytical grade acids, with a subsequent stepped heating program up to 170 °C overnight, to digest silicate and oxide phases. The dry residue was re-constituted after warming with Milli-Q water, HNO_3 and H_2O_2, to 25 ml of 5% v/v HNO_3 and stored in HDPE bottles. Reference materials (NIST SRM2710, SRM2711, GSS-6, BGS102 and BCR-2), duplicated samples and blanks were all prepared in a similar manner to check accuracy of the analytical and digestion method. In addition to the quantification of P$_{\mathrm{Total}}$, a range of elements associated with P mineralogy and phosphate sorption were measured including Al, Fe, Mn and Ca by ICP-MS. P$_{\mathrm{Labile}}$ was determined using an equilibrating solution of 0.5 M $NaHCO_3$ adjusted to pH 8.5 on the air-dry samples from each of the homogenised cores. Triplicate samples were shaken in a 1:20 sediment:solution ratio for 30 min before centrifuging at 1327 RCF for 15 min and filtering (0.45 μm). Analysis was carried using the molybdenum blue method (Murphy and Riley, 1962) and the results expressed on an oven dry weight basis. Estimates of amorphous and poorly crystalline oxyhydroxides of Fe (FeOOH), Mn (MnO_x) and Al (AlOOH) in sediment were determined using 0.2 M ammonium oxalate and 0.125 M oxalic acid extractions. Samples were shaken in darkness for 2 h (McKeague and Day, 1966) (see Supplementary Information 1 for additional information). Particle size distribution (PSD) of sediment samples (0.01–2000 μm) was determined using a Beckman Coulter LS13 320 laser diffraction particle size analyser. Prior to analysis, organic matter was removed using H_2O_2. Mineralogy of the sediments was examined using Scanning Electron Microscopy (SEM) and Scanning Transmission Electron Microscopy (STEM) (see Supplementary Information 2 for methodologies and results).

2.6. Solution analysis

Phosphate concentrations in (a) river water samples (b) Olsen P extracts, (c) isotherm analysis and (d) kinetic analysis were undertaken using the molybdenum blue method (Murphy and Riley, 1962). Calibration curves and analysis were undertaken using a Perkin Elmer Lambda 35 uv/vis spectrometer. Limits of Detection (LOD) were calculated for each of the different matrices and were 0.22 μg P for water, 0.37 μg P for 2 mMol $CaCl_2$ and 0.59 μg P for the 0.5 M $NaHCO_3$ Olsen P extractions. Total elements in water samples collected were analysed by ICP-MS.

2.7. Methodologies for EPC$_0$ and rates of desorption or sorption

When considering the dynamics of the interactions of SRP with river sediment, it is important to know whether the sediment has the potential to act as a source or a sink. The EPC$_0$ represents the equilibrium concentration of SRP in solution (i.e. when there is no net sorption or desorption in a laboratory simulation undertaken over a 24 h period). Thus, when SRP concentrations in the overlying water are greater than EPC$_0$, the sediment has the potential to sorb SRP from the water column and act as a sink. By contrast when SRP concentrations are less than the EPC$_0$, the sediment has the potential to release SRP to the water column and act as a source. EPC$_0$ analysis was undertaken on wet sediment (0–5 cm) within seven days of sampling to minimize sample deterioration as suggested by Jarvie et al. (2005). A measured mass of sediment (equivalent to 0.5 g dry weight) was placed in 6 bottles with 200 ml of a synthetic water composition roughly matching the major element chemistry of the River Nene (2 mmol $CaCl_2$). The bottles were spiked with different concentrations of KH_2PO_4 (the amounts of P added were equivalent to 0, 2.5, 5, 10, 15 and 20 μmol l^{-1}), and placed in an orbital shaker in the dark at 10 °C for 24 h. Samples were then centrifuged and their SRP concentration determined (Murphy and Riley, 1962). The isotherms produced were based on the Freundlich model (Equation (2)) which was fitted using the least squares method. The Freundlich model takes the form

$$\Delta \boldsymbol{N_a} = \boldsymbol{K_f C_i^n} \tag{1}$$

where ΔN_a = change in adsorbed P (μmol g^{-1}), K_f is the Freundlich constant, C_i is the concentration of SRP in solution and n is a constant. Using the fitted isotherms the Equilibrium Phosphorus Concentrations (EPC$_0$) was calculated for each sample (see House et al., 1995; Jarvie et al., 2005). The EPC$_0$ and SRP measurements were compared using an 'EPC$_0$ percentage saturation' term (EPC$_{0\text{-sat}}$) calculation, which describes the increase or decrease in SRP compared to the EPC$_0$. This is defined as

$$\mathrm{EPC}_{0\mathrm{Sat}}(\%) = 100{*}(\mathrm{EPC}_0 - \mathrm{SRP})/\mathrm{EPC}_0 \tag{2}$$

2.8. Calculation of rate constants for SRP sorption/desorption from sediments

To calculate the rate of release or sorption of SRP from/to sediments, the kinetic methodology described by Jarvie et al. (2005) was used. For the SRP release experiments (where EPC$_0$ > dissolved SRP), a measured mass of wet sediment (equivalent to 0.5 g dry sediment) was placed in polypropylene bottles with 200 mL of $CaCl_2$ solution, pre-chilled to 10 °C. For SRP uptake experiments (where SRP > EPC$_0$), the synthetic river solution in each bottle was spiked with KH_2PO_4 to an appropriate SRP concentration (greater than the EPC$_0$ and close to the measured SRP concentration in the water column at the time of sediment sampling). For water body 1 & 2, a 2 μM P solution was used and for the other 4 water bodies a 4 μM P equilibrating solution was used, these concentrations being slightly greater than those measured in the river waters at the time of collection. Bottles were placed in an orbital incubator in the dark and shaken at 150 rpm at 10 °C and then one bottle was sampled after specific time intervals (5 min, 15 min, 30 min, 1 h, 3 h, 6 h, 15 h, 24 h), centrifuged and analysed for their SRP concentrations. The sorption/desorption rates of SRP (House and Warwick, 1999; Jarvie et al., 2005) to or from the sediments were calculated based on the equation:

$$\boldsymbol{R} = \boldsymbol{K_r}(\boldsymbol{C_t} - \boldsymbol{C}_0)^n \tag{3}$$

R is the change in amount of orthophosphate sorbed (μmol g^{-1} h^{-1}), C_t is the orthophosphate concentration (μmol l^{-1}) in the overlying water, C_0 is the orthophosphate concentration in the overlying water after 24 h (μmol l^{-1}), K_r is a rate constant (μmol^{1-n} l^n g^{-1} h^{-1}) and *n* is a power term. The Nelder–Mead algorithm as implemented in Matlab (Lagarias et al., 1998) was used to determine the parameter values by minimizing the squared difference between the observed concentrations and those predicted by the rate curve.

2.9. Statistical analysis

Multiple linear regression by ordinary least squares was used to examine the geochemical and environmental controls on P_{Total} and oxalate extractable P in the river sediments. Based on previous research, there are geochemical associations (e.g. concentrations of Mn, Fe and Al or oxalate extractable components of them) which may account for the variation in total sediment P or its reactive components (e.g. $P_{Oxalate}$). The relative importance of these associations accounting for P_{Total} and $P_{Oxalate}$ were investigated by including the concentrations of specific elements or their extractable components as predictors in regression models and exploring the interactions between the geochemical predictors using the linear model (*lm*) function in the R statistical environment. After initial analysis of the data, and to improve the model, each sample point was allocated to one of two parts of the river system (water bodies 1–3 or water bodies 4–6) and this was included within the regression model. This allocation represented whether water bodies were in a rural (water bodies 1–3) or more urbanised (water bodies 4–6) part of the catchment. The reasons why this allocation was undertaken is explained in Section 3.3. In each case we checked that the residuals from the models were approximately normally distributed.

3. Results and discussion

3.1. Sediment distribution and depth in the River Nene

Few detailed descriptions of sediment depth and distribution for relatively deep (~2 m) rivers in the UK exist, although some have been published for shallow chalk bed rivers (e.g. Cotton et al., 2006). The generalised patterns of sediment distribution, found in each water body of the Nene at the time of sampling and after the period of flooding and high river flow (Section 2.4) were as follows. For water bodies 1, 2, and the top part of water body 3, sediment deposition at the sampling sites generally consisted of gravel and sand, although an occasional silt deposit was found in areas of slower flow, particularly on sharp bends or where field drainage entered the channel. For water bodies 3–6, most sediment deposits located extended <1 m into the water channel and were largely confined to small inlet areas of the river channel where the current was slower. No fine grained sediment deposits were found in the central areas of the main channel, with probing only revealing a compact armoured bed. It is not clear to what extent the absence of sediment along much of the river channel was a function of the extended period of flooding and high river flow that was prevalent throughout the winter period of 2012/13 that preceded sampling. However, large areas of macrophyte vegetation had been removed by the flooding throughout the length of the river, allowing greater sediment removal (Cotton et al., 2006). Previous work has recorded that extensive scouring of sediment can occur in the River Nene as a consequence of long periods of flooding and high water flow with the resultant removal of significant macrophyte communities (Brierley et al., 1989). A visit to sampling sites in the spring of 2013 showed the areas from which sediment was sampled for this work was usually the substrate for macrophyte (e,g, *Iris pseudacorus*) growth and it is likely that the root systems prevented erosion of this sediment. Typically in water bodies 1 & 2 the mean depth of the sand and gravel lag was <10 cm to the clay river bed. Water bodies 3–6 had sediment deposits with a mean of ~60 cm. However, large standard deviations demonstrate the variability of mean sediment depth within each water body (see graph 1 in Supplementary Information 3).

3.2. Sediment properties

Particle size distribution (PSD < 2 mm) was analysed in the homogenised samples from each water body and plotted on a ternary diagram, along with estimates of particle size from the soils derived from the major soil parent materials (Dyrham mudstone, Charnmouth mudstone, Whitby mudstone and the alluvial floodplain soils) in the catchment (Fig. 2). Particle size varied between 6 and 91% for sand, 4–35% for silt and 2–66% for clay for the homogenised cores taken from the six water bodies. The percentage of stones by weight (>2 mm) in the samples were from 0 to 30%

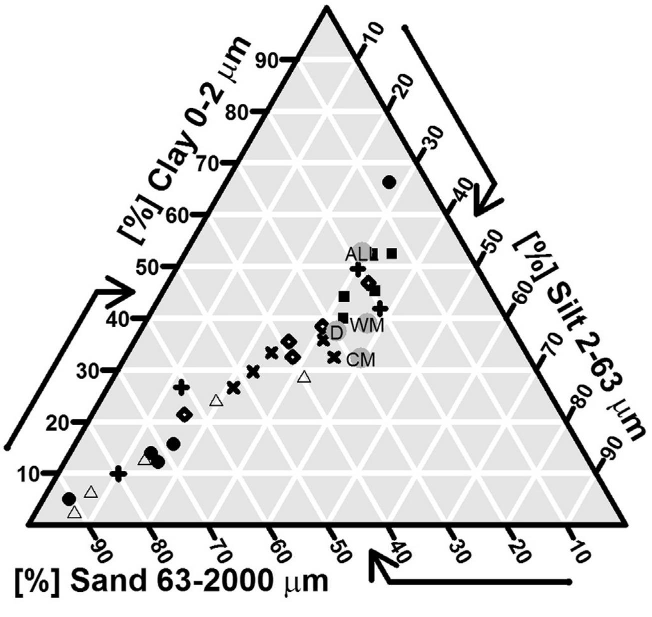

Fig. 2. Particle size distributions of homogenised samples (n = 30) from the river Nene channel and soils derived from major soil parent materials from the catchment. Sediments are marked as (●) for Water Body 1, (△) for Water Body 2, (+) for Water Body 3, (×) for Water Body 4, (■) for Water Body 5 and (◊) for Water Body 6. Particle size of the soils derived from the parent materials that make up the Nene catchment are marked as ALL = Alluvial soils, D = Dyrham Formation, CM = Charnmouth Mudstone, and WM = Whitby Mudstone formation.

with a median value of 2.98%. A higher percentage weight of stones was found in the samples taken from sand and gravel sediments in water bodies 1–3 where coring was not possible, with the range being 0–30% with a median of 8.6%. In water bodies 4–6 the range for the weight of stones in the sediment cores was 0–22% with the median being 0.5%. Sediments in water bodies 1–3 were generally coarser than the soils, suggesting transport of finer particles downstream. A general, but with occasional exceptions, fining in PSD occurred in each water body as distance from the headwaters increased but the variability within each water body demonstrates that the major influences on the particle size distributions is the depositional environment (e.g. position in relation to current, density of plants that can trap sediment, sediment input). However, the PSD of the cores generally did not become finer than the alluvial soil within the catchment, but 7 out of the 30 sediment samples became finer to varying degrees than the soil generated directly from the mudstone parent materials.

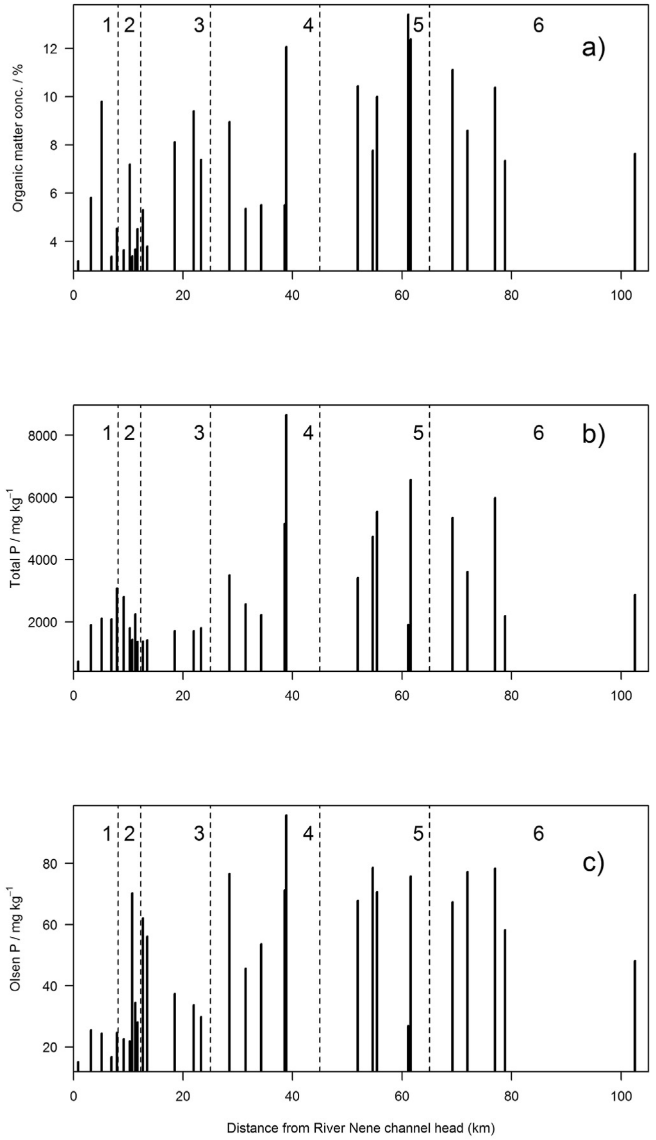

Fig. 3. Changes in (a) organic matter as determined by loss on ignition (%), (b) Total sediment P (mg kg^{-1}) and (c) Olsen extractable P (mg kg^{-1}) for the 5 homogenised samples collected from the six water bodies of the River Nene. The end of each water body is marked by the broken vertical line and the sampling points are measured as distance from the channel head.

Organic matter content (LOI) varied between 3.18 and 12.06% in the homogenised cores taken from the six water bodies. Fig. 3 shows that % LOI tends to be higher after water body 2. The results are generally associated with the % clay in the samples. A linear regression between LOI and % clay was found (% LOI = 3.05 + 0.145% Clay; df = 29; $r^2 = 0.65$, $P < 0.001$). This is possibly a result of slower water currents enabling greater quantities of fine silt and clay particles to settle; these along with FeOOH and AlOOH being the particles that organic matter tends to sorb in soils and sediments. Weaker regression relationships were found between $Fe_{Oxalate}$ (% LOI = 2.88 + 0.0002 $Fe_{Oxalate}$; $r^2 = 0.42$; df = 29; $P < 0.001$) or $Al_{Oxalate}$ (% LOI = 1.712 + 0.0034 $Al_{Oxalate}$, $r^2 = 0.46$ df = 29; $P < 0.001$) and (% LOI where oxalate concentrations are in mg kg^{-1}).

3.3. *P_{Total} in homogenised sediment cores*

Concentrations of P_{Total} was analysed in the homogenised sediment cores and results are shown in Fig. 3. An increase in P_{Total} was found after core 18, the end of water body 3. The whole P_{Total} dataset was assessed along with particle size, organic matter and elements (Ca, Mg, Fe and Mn) commonly associated with P bearing minerals or sorptive surfaces. Initial correlation analysis suggested no relationships existed between P_{Total} and these parameters. However, when the data was plotted there were indications that separate relationships existed between the upper water bodies (1–3) and lower water bodies (4–6). In particular, relationships were found between P_{Total} and Fe_{Total} and Mn_{Total} (Fig. 4).

Four possible explanations were considered for the relationships found between P_{Total} and Fe_{Total} or Mn_{Total} for the two sets of grouped water bodies, these being; (i) a change in geology with associated changes in the geochemistry of sediment inputs (soil) to the river, (ii) a change in agricultural practice, (iii) changes caused by the fining of the sediment as previously described and (iv) a change from a rural catchment to a more urban catchment, with associated increases in SRP inputs from STW's, particularly from

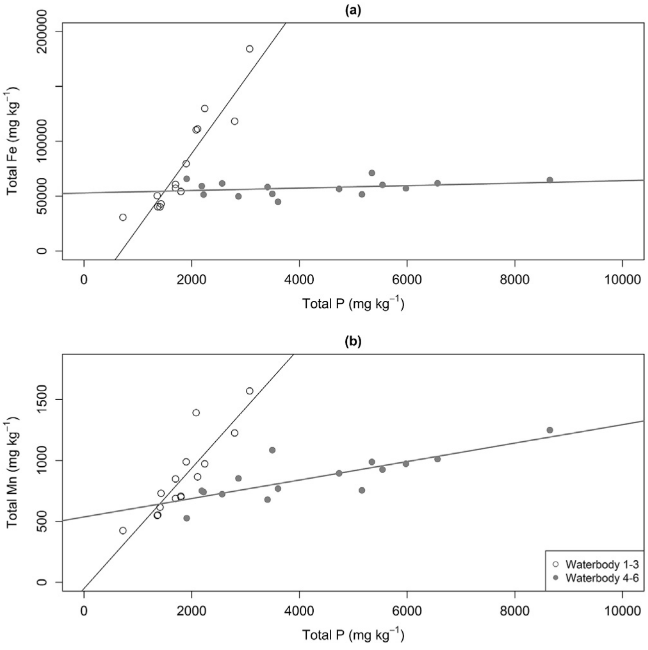

Fig. 4. Relationships between P_{Total} (mg kg^{-1}) and (a) Total Fe (mg kg^{-1}) and (b) Mn_{Total} (mg kg^{-1}) in the 5 homogenised sediment samples taken from each of the six water bodies of the River Nene.

Northampton onwards as the population size in the catchment increases. The change in geology was considered as the Dyrham mudstone changed to the Whitby mudstone formation around the end of water body 3; this may have provided changes in the geochemical relationships of the soils. Using data obtained from the BGS G-BASE geochemistry survey (Johnson et al., 2005), Cumulative Distribution Functions (CDF) for Mn, Fe and P were plotted for soils formed from the two major soil parent materials (Dyrham and Whitby mudstones) in the Nene catchment to allow comparisons of the concentration ranges. Thus, considering explanation (i) above, only small differences were found in the concentration ranges of P, Fe and Mn from soils formed from the two major soil parent materials (Fig. 5). The largest difference found was that in the Whitby soil where there was an increase in Fe_{Total} and P_{Total} above the 60th percentile compared to the Dyrham soil. Thus these CDF's suggest that the geochemical properties of the soil inputs to the river were broadly similar. The second explanation was based on an increase in arable agriculture within the catchment. Land cover maps of the Nene catchment to the west of Peterborough show that it is predominately arable agriculture. There is a slight increase in the area of improved pasture in the land associated with water bodies 1–2 but arable agriculture is still the major land use (EA, 2014).

The third explanation to be considered was that particle size differences caused changes in element concentration through fining. Firstly, eroding soil has been found to selectively transport fine particles (Sharpley, 1980; Warrington et al., 2009) and this process can also continue within the river. Both these processes concentrate P because fine particles have a greater surface area per unit weight, and oxides are often associated with clay particles. For example Miller et al. (2009) found that P was concentrated up to ~4 times in a selection of artificially eroded soils. By examining the PSD of the Nene sediments in comparison to the catchment soils, it is evident that there has been some loss of fine particles from water bodies 1–3. However, very few of the sediment samples had a PSD finer than the catchment soils, particularly in water bodies 4–6, suggesting that increases in P enrichment were not solely due to an increase in fine particles in the sediment samples. Both PSD data and CDF's were used to examine changes between the soil and sediment. For water bodies 1–3, the shape of the sediment CDF shows that an increase in sediment Fe_{Total} was found in the upper 40% of samples whilst a small increase in P_{Total} occurred compared to the soil parent material (Fig. 6), despite a coarsening of particle size. For the increase in Fe_{Total} compared to the soil, a likely explanation is that the loss of the fine particles from the sediment

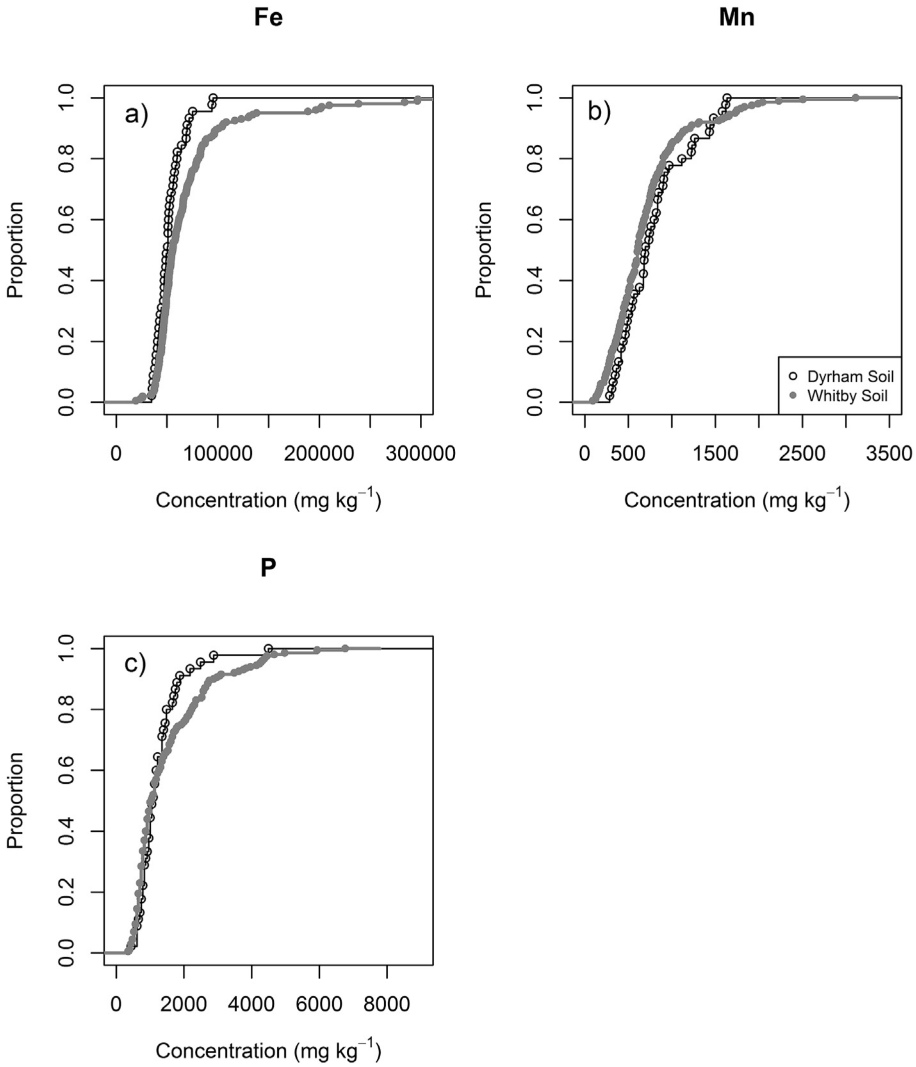

Fig. 5. Cumulative Distribution Functions to describe the range of (a) Fe_{Total}, (b) Mn_{Total} and (c) P_{Total} concentrations in soils above the two main soil parent materials, the Dyrham and Whitby mudstones.

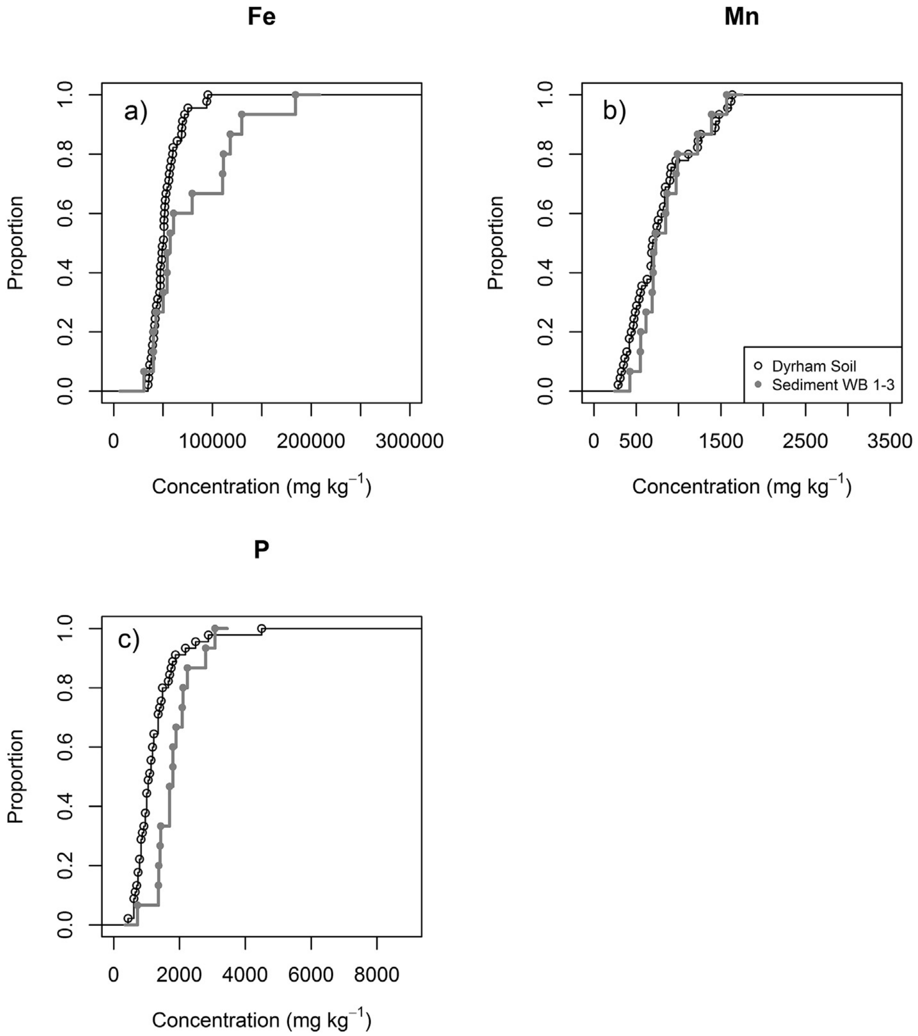

Fig. 6. Cumulative Distribution Functions to describe the range of (a) Fe_{Total}, (b) Mn_{Total} and (c) P_{Total} concentrations in soils and sediments (<2 mm) in water bodies 1–3 of the River Nene where the dominant soil parent material is the Dyrham mudstone.

may have increased the relative concentration of Fe_{Total} because the sand particles were covered in iron oxides. All the samples with the highest Fe_{Total} concentrations in the dataset came from these sand and gravel lag samples and not the homogenised cores (see Section 2.4). The small increase in P may reflect the binding of P to these FeOOH coverings from the soil or some in-situ sorption from the river water.

For water bodies 4–6, increases in the ranges of Fe_{Total} and Mn_{Total} were confined to the upper 10th percentile in the soil as compared to the sediment (Fig. 7). However, a considerable enrichment in P_{Total} was found in the sediment, as compared to the soil parent material. As the PSD of the soils is not all that different to many of the sediments in water bodies 4–6, the suggestion is that a large proportion of this enrichment was caused by in-situ sorption of SRP from the water. Whilst agriculture (e.g. fertilisers, direct livestock inputs) is a likely contributor, the probable major source is SRP released via the STW's. The position of STW's that discharge to the river Nene are marked on Fig. 1. In particular it is STW output that is discharged to the Nene from the major urban areas of Northampton, Wellingborough and Kettering that are likely to cause this enrichment. An indication of the size and potential quantity of P discharging from the STW's serving these towns can be gauged by their population sizes of 65,000, 25,000 and 41,000 respectively. By comparison the population of Daventry the biggest town in the Nene catchment in waterbodies 1–3 is 8000 (NVNIA, 2013). Thus, there is a strong suggestion that P enrichment particularly in the sediments of water bodies 4–6 appears to be from in-situ sorption of SRP and the greater urban influence within a still predominantly rural catchment. Further evidence for STW's being the source of the sediment P enrichment is found in the relationship between SRP and Boron. Table 1 reports SRP and Boron concentrations in the river water samples collected at the $Core_D$ locations. Concentrations of SRP were between 0.18 and 4.63 μm P L^{-1}. Boron is used as a whitener in washing powder and has been used as a tracer to determine whether SRP is derived from agriculture or STW's. Typical background concentrations of Boron in river waters are generally <30 μg L^{-1} (Jarvie et al., 2005, 2006; Neal et al. 2010). In this study, despite the small number of sample points there was a positive linear correlation of ($r = 0.80$) suggesting that the SRP in the river water may be largely linked to discharges from STW's. The increasing concentrations of SRP and Boron were both found with increasing distance from the headwaters of the Nene, and are likely a result of the increasing numbers or size of STW's feeding water into the river system as shown in Fig. 1.

Overall the relationship between P_{Total} and Fe_{Total} and Mn_{Total}

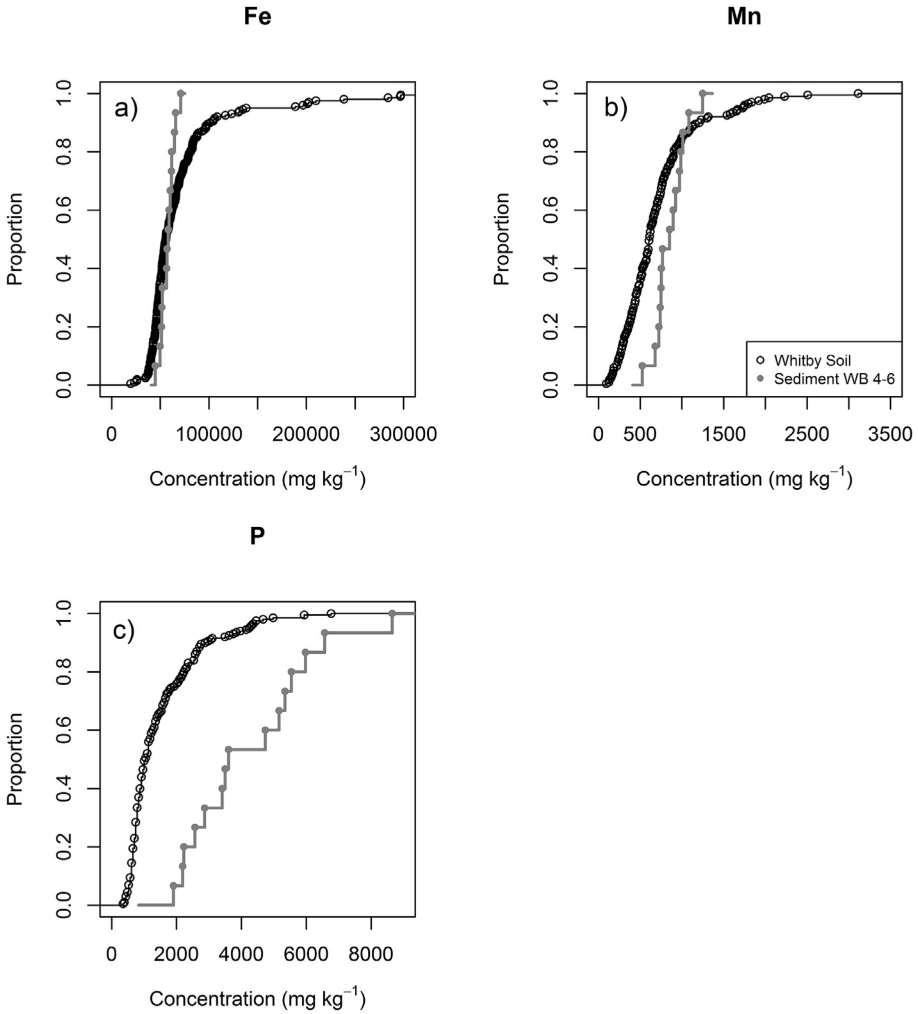

Fig. 7. Cumulative Distribution Functions to describe the range of (a) Fe_{Total}, (b) Mn_{Total} and (c) P_{Total} concentrations in soils and sediments in water bodies 4–6 of the River Nene where the dominant soil parent material is the Whitby mudstone.

appears to differ between water bodies 1–3 and water bodies 4–6 because of the likely increase in STW inputs as population size increases and the catchment becomes less rural. A regression model for the prediction of P_{Total} was parameterised. The best fit model was parameterised using Mn_{Total} concentration and the rural/urban catchment influence (with an interaction between them) as predictors and accounted for 78% (adjusted R^2) of the variation in P_{Total} (Table 2); the two lines are for the rural/urban catchment classes for water bodies 1–3 and 4–6 and the two regression equations are as follows:

$$P_{Total}(\text{wb}\ \ 1,2,3) = 4580 + 1.61{*}Mn_{Total} \tag{4}$$

$$P_{Total}(\text{wb}\ \ 4,5,6) = 4580 - 3414 + 1.61{*}Mn_{Total} + 6.80{*}Mn_{Total} \tag{5}$$

3.4. P associations with mineral phases and amorphous oxides

SEM and STEM analysis was undertaken on sediments. Minerals phases associated with anaerobic conditions in the sediment were identified in the core samples. These minerals included vivianite ($(Fe^{2+})_3(PO_4)_2 \cdot 8H_2O$), siderite (FeCO3) and Ca–Mn-Carbonate. Fe oxide minerals were associated with clay minerals and mixed MnO_x–FeOOH coatings were found (See Supplementary Information 2; Figs. 1–3 for images of mineral phases). The concentration and composition of amorphous oxides is likely to be influenced by the dissolution and re-precipitation, and redox reactions of mineral phases during aerobic–anaerobic cycles within the sediment architecture. Table 3 reports concentration ranges and median values of oxalate extractable Al, Fe and Mn. Concentration ranges of $Al_{Oxalate}$, $Fe_{Oxalate}$ and $Mn_{Oxalate}$ were higher in water bodies 4–6 compared to water bodies 1–3. During precipitation of the oxyhydroxides, phosphate ions may become incorporated within their structures. By measuring $P_{Oxalate}$ release the importance of amorphous oxides in binding P is demonstrated. Whilst most of the P released from this extraction will be P that has been incorporated within the oxalate extractable oxides, it is possible that a small amount of organic P that binds to the surface of these oxides (Jiang et al., 2015) will be also be released during the extraction. This demonstrates the importance of amorphous oxides to binding both inorganic or organic P species. The mean percentage of P_{Total} that $P_{Oxalate}$ equated to was 31, 59, 74, 89, 94 and 90% for water bodies 1 to 6 respectively indicating that a greater proportion of P was oxalate extractable as distance from the headwaters increases.

Linear regression relationships between $P_{Oxalate}$ and $Fe_{Oxalate}$

($P_{Oxalate} = -947 + 0.139^{*}Fe_{Oxalate}$; $r^2 = 0.50$; df = 29; $P < 0.001$), $Al_{Oxalate}$ ($P_{Oxalate} = -1129 + 2.42^{*}Al_{Oxalate}$; $r^2 = 0.45$; df = 29; $P < 0.001$) and $Mn_{Oxalate}$ ($P_{Oxalate} = -1066 + 7.351\ ^{*}Mn_{Oxalate}$; $r^2 = 0.25$; df = 29; $P < 0.01$) were found, indicating that all three oxides (mg kg^{-1}) contribute to the sorption and fixation of P. Concentrations of $P_{Oxalate}$ were predicted using regression analysis to assess the factors determining its concentrations in the river sediment. The predictors in the optimum regression model accounted for 78% (adjusted R^2) of the variance (Table 4). In the best fit model (Fig. 8) $Mn_{Oxalate}$ was significant ($P < 0.05$) as was the term water bodies 4,5,6:$Fe_{Oxalate}$ ($P < 0.001$). This latter term was significant because of the large increase in $Fe_{Oxalate}$ concentrations in waterbodies 4–6, compared to waterbodies 1–3 (Table 3) and its role as the dominant P sorbing surface. However, there was strong predictive power demonstrated by $Mn_{Oxalate}$ although its concentration is up to two orders of magnitude lower than that of $Fe_{Oxalate}$. A parameter for differentiating between the more rural and urban catchments was included (Waterbodies 4, 5 & 6) although this was not significant. The two equations predicting $P_{Oxalate}$ (from Table 4) are:

$$P_{Oxalate}(\mathrm{wb}\ 1,2,3) = -1404 + 0.046^{*}Fe_{Oxalate} + 3.395^{*}Mn_{Oxalate} \quad (6)$$

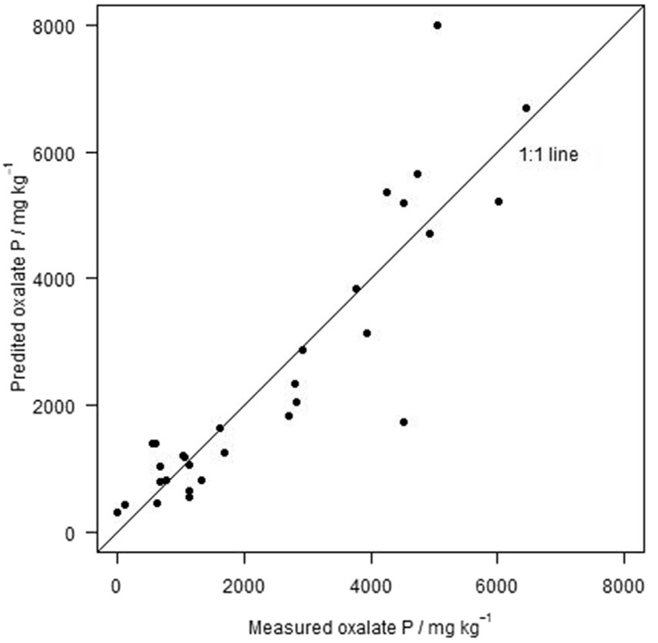

Fig. 8. Scatterplot of measured and predicted concentrations of $P_{Oxalate}$ in Nene sediments based on the significant predictors (urban or rural catchment class, the concentration of $Fe_{Oxalate}$ with respect to water body and $Mn_{Oxalate}$ concentration) and their interactions.

Table 1
Parameters obtained from isotherm fitting analysis to calculate Equilibrium Phosphate Concentration (EPC_0) in samples from each of the water bodies of the river Nene based on Equation (1) and EPC_{0Sat} calculated using Equation (2).

Sample	F	k	RSS	EPC_0 (µm P L^{-1})	EPC_{0Sat} (%)	k_d L kg^{-1}	SRP (µm P L^{-1})	Boron (µg L^{-1})
Water body 1	43.9	0.008	0.03	1.31	87.59	33	0.18	41
Water body 2	52.2	0.029	0.44	0.61	−180	249	1.65	52
Water body 3	176	0.048	2.33	0.85	−444	3743	4.63	53
Water body 4	413	0.027	2.78	1.19	−185	4286	3.40	61
Water body 5	403	0.055	9.56	1.67	−160	8445	4.35	81
Water body 6	296	0.023	1.50	1.69	−126	1555	3.83	79

Table 2
Results of the regression model fitted by ordinary least squares for the prediction of total sediment P concentrations in the River Nene sediments.

	Estimate	Standard error	t-value	*P*-value
Intercept	4580	653	0.702	0.489
Total Mn	1.61	0.717	2.24	0.034
[a]Water bodies 4,5 & 6	−3413	1298	−2.63	0.142
[b]Total Mn: Water bodies 4, 5 & 6	6.80	1.46	4.64	<0.001

[a] Denotes the ‘urban’ based catchments class for water bodies 4, 5 & 6. The estimate of the regression coefficient (slope) is the difference from the estimated coefficient for the rural class underlying water bodies 1, 2 & 3.

[b] Interaction between Total Mn and WB 1–3 (rural) and WB 4–6 (urban) based catchments.

Table 3
Oxalate extractable concentrations ranges and median concentrations for Al, Fe and Mn in sediments of the River Nene.

	Water bodies 1–3 (mg kg^{-1})	Water bodies 4–6 (mg kg^{-1})
$Al_{Oxalate}$: range	429–2060	987–2373
Median	890	1804
$Fe_{Oxalate}$: range	9324–39,000	15,846–40,543
Median	13,454	32,300
$Mn_{Oxalate}$: range	228–644	275–753
Median	383	515
$P_{Oxalate}$: range	305–1634	1402–7995
Median	828	3842

Table 4
Results of the regression model fitted by ordinary least squares for the prediction of total sediment oxalate extractable P concentrations in River Nene sediments.

	Estimate	Standard error	t-value	*P*-value
Intercept	−1404	531	−1.42	0.167
[a]Water bodies 4,5 & 6	−1848	1354	−1.36	0.1845
$Fe_{Oxalate}$	0.046	0.027	1.68	0.105
$Mn_{Oxalate}$	3.395	1.507	2.25	<0.05[a]
[b]Water bodies 4,5,6:$Fe_{Oxalate}$	0.1311	0.050	2.61	<0.01[b]

[a] Denotes the urban/rural class for waterbodies 4, 5 & 6. The estimate of the regression coefficient (slope) is the difference from the estimated coefficient for the rural (WB1-3)/urban (WB 4–6) influenced catchment class underlying waterbodies 1, 2 & 3.

[b] Interaction between $Fe_{Oxalate}$ and WB 1–3 and 4–6.

$$P_{Oxalate}(\mathrm{wb}\ 4,5,6) = -1401 - 1848 + 0.046\ Fe_{Oxalate} + 3.395 * Mn_{Oxalate} + 0.1311 * Fe_{Oxalate} \quad (7)$$

The degree of P saturation (DPS) can be calculated as a measure of how saturated the P sorbing surfaces are with P. It is calculated using the oxalate concentrations (Moles) because they are the major sorptive surfaces. Thus DPS = $P_{Oxalate}/(Al_{Oxalate} + Fe_{Oxalate} + Mn_{Oxalate})$. The mean concentration of sorbing surfaces was 0.32, 0.37, 0.42, 0.59, 0.69 and 0.58 M for water bodies 1–6 respectively, mirroring the previously described increase in oxalate surfaces as distance increases from the headwaters. Results show that mean DPS for water bodies 1–6 respectively are 5.87, 10.15, 10.19, 20.70, 19.33 and 19.74%.

3.5. *Labile P in sediments*

Concentrations of P_{Labile} for the samples taken from each water body are shown in Fig. 3. Mean values for each water body are shown in Supplementary Information 3, Fig. 2. Results show a trend of increasing P_{Labile} concentrations from water body 1 through to water body 6. Concentrations of P_{Labile} varied between ~17 and 100 mg kg^{-1}, these typically being <5% of P_{Total} in all instances with most samples being <2%. P_{Labile} concentrations were examined in the $Core_D$ samples with maximum concentrations being ~60 mg kg^{-1}. There was little evidence of a systematic pattern of P_{Labile} deposition with depth in these six samples from different water bodies, with concentrations of P_{Labile} being in a similar range to those from the homogenised cores.

There were no statistical relationships found between P_{Labile} and LOI, Fe_{Total}, Al_{Total} and Mn_{Total}. Relationships between P_{Labile} and the oxalate extractable elements were examined. The $P_{Oxalate}$ pool (range 0–7995 mg kg^{-1}) was much greater than the P_{Labile} pool (0–100 mg kg^{-1}), demonstrating the degree to which P has been fixed within the amorphous oxide minerals. For the homogenised core samples, no linear relationships were found between P_{Labile} and $Fe_{Oxalate}$ or $Al_{Oxalate}$ although numerous reports have suggested strong relationships in soils and sediments (e.g. Hartikainen et al., 2010). However, Fig. 9 shows a linear regression relationship between P_{Labile} and $Mn_{Oxalate}$ for the homogenised cores that accounted for 63% of the variation in P_{Labile} in sediments (Table 5). In this instance the rural/urban catchment classification was not significant. The mean values of P_{Labile} and $Mn_{Oxalate}$ from the $Core_D$ samples are included in the graph and fall within the homogenised core data.

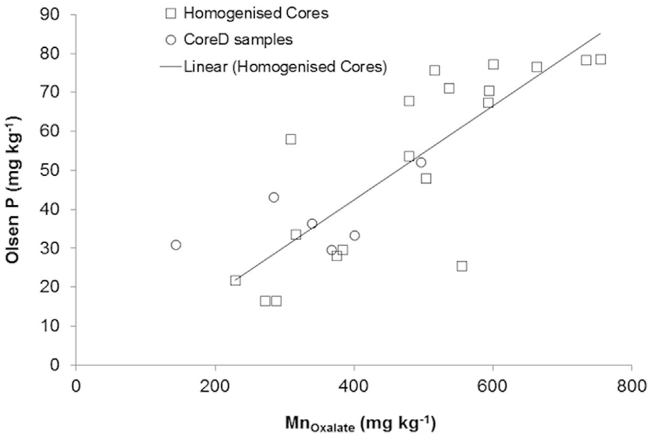

Fig. 9. Relationship between P_{Labile} and $Mn_{Oxalate}$ for the homogenised cores and the mean values of P_{Labile} and $Mn_{Oxalate}$ for $Core_D$ samples.

Table 5
Results of the regression model fitted by ordinary least squares for the prediction of P_{Labile} in sediments.

	Estimate	Standard error	t-value	*P*-value
Intercept	−3.973	8.242	−0.48	0.63
$Mn_{Oxalate}$	0.1125	0.017	6.62	<0.001

3.6. *Controls on the Equilibrium Phosphorus Concentration*

Using the top 5 cm taken from $Core_D$ from each water body, the 'Equilibrium Phosphorus Concentration' was determined. The EPC_0 is primarily a function of the sediment properties that contribute to surface charge such as the particle size distribution, surface area, oxide concentrations, organic matter and water properties such as electrical conductivity (as a proxy for ionic strength) and pH. Concentrations of EPC_0 for the six water bodies of the River Nene were between 0.61 and 1.69 μm P L^{-1} (Table 1) with the greatest values being found in water bodies 5 and 6. Placing these results within the context of other reported results, Hartikainen et al. (2010) found EPC_0 between 0.09 and 10.84 μm L^{-1} for a range of soils and sediments, whilst Jarvie et al. 2005 recorded values of between 0.06 and 5.74 μm L^{-1} (median = 1.36 μm L^{-1}) for sediments in the Hampshire Avon (predominantly chalk) catchment and 0.03 and 6.29 (median = 0.71 μm L^{-1}) for the Wye catchment (mudstone). Stutter and Lumsdon (2008) found EPC_0 values of between 0.03 and 1.75 μm L^{-1} (median = 0.195) for the River Dee catchment where soils are largely derived from granites and acid schists.

Comparison of the EPC_0 with the SRP concentration determined in the water sample taken at each site (Table 1) show that only in water body 1 does the EPC_0 exceed the SRP in the water sample, thus suggesting that the sediment is a source of SRP. However, when the kinetic analysis was undertaken the sample was found to sorb rather than release SRP. This sample was the first to be taken after the floods and the river flow was still very high, so it is possible that equilibrium between SRP and sediment had not yet been reached. Therefore all examined sediments of the Nene were capable of uptake SRP from the water column, and this is similar to the majority of studies from the UK (e.g. House and Denison, 1997; House and Denison, 1998; Jarvie et al. 2006). The negative values of EPC_{0Sat} after water body 1 (Table 1), suggest that there is considerable under saturation of the EPC_0 with SRP suggesting that the sediment has considerable capacity to absorb further SRP.

The values of EPC_0 were examined in conjunction with the sediment properties that may control the sorption and desorption of SRP. There was no relationship between P_{Labile} and EPC_0, suggesting that the P_{Labile} assay used may deplete the whole labile pool and not just the least strongly held part of P_{Labile} that it actively buffering the solid-solution equilibria. There were no correlations between $Al_{Oxalate}$, $Fe_{Oxalate}$ or $Mn_{Oxalate,}$ and the values of EPC_0.

3.7. *Determining kinetic constants for P uptake*

Rate constants were determined for the 0–5 cm segments of $Core_D$ taken from each water body. All sediments tested showed a rapid absorption of SRP (see Tye et al., 2013 for graphs), with a pseudo-equilibrium generally being reached within one hour (C_0 in Table 6). This rapid response has been found by others (e.g. Jarvie et al., 2005). The concentration of C_0 (effectively the point of zero net sorption or desorption) was very similar to the value obtained for EPC_0 previously (Table 1). Rate co-efficients (K_r) for SRP uptake

Table 6
Outputs from the kinetic experiments where (K_r) is the kinetic rate constant ($\mu mol^{1-n}\ l^n\ g^{-1}\ h^{-1}$), C_0 is the orthophosphate concentration in the overlying water after 24 h ($\mu mol\ l^{-1}$), and n is a power term for sediment (0–5 cm) from each of the 6 $core_D$ samples collected from each of the water bodies of the River Nene. Values of K_r, C_0 and n calculated using Equation (3).

	K_r $\mu mol\ l^{l-n}\ g^{-1}\ h^{-1}$	C_o	n
Waterbody 1	2.366	1.363	2.05
Waterbody 2	51.714	0.623	2.16
Waterbody 3	10.687	0.662	1.09
Waterbody 4	25.477	1.117	1
Waterbody 5	26.954	1.45	1.26
Waterbody 6	14.113	1.89	2.29

varied between 2.36 and 51.71 $\mu mol\ l^{1-n}\ g^{-1}\ h^{-1}$ (Table 6) for the six water bodies. These values are within the range of previously published uptake rate constants including an average rate constant of 10.6 $\mu mol\ l^{1-n}\ g^{-1}\ h^{-1}$ (range 0.84–54) for the Hampshire Avon catchment and a mean of 4.96 $\mu mol\ l^{1-n}\ g^{-1}\ h^{-1}$ (range 0.54–18.9) for the Wye catchment (Jarvie et al., 2005). The values of K_r were examined in respect to surfaces that may sorb SRP. Both $Fe_{Oxalate}$ ($r = 0.91$) and $Al_{Oxalate}$ ($r = 0.91$) demonstrate a strong positive correlation with K_r, if the value (51.71 $\mu mol\ l^{1-n}\ g^{-1}\ h^{-1}$) for water body 2 is not included, suggesting that these oxides are important in SRP sorption from the water (see Supplementary Information 3; Fig. 3). Investigating why water body 2 does not fit this relationship demonstrates that K_r is determined by a combination of both sediment texture and oxide concentration. This sample had 48% clay (the range in the other samples was between 13 and 42%) but had the second lowest concentrations of $Fe_{Oxalate}$ and $Al_{Oxalate}$. Thus in this instance it was likely that the clay surfaces compensated for the lower $Fe_{Oxalate}$ and $Al_{Oxalate}$ concentrations in the sorption of SRP.

3.8. General discussion

Within the main channel of the river Nene, major sediment inputs include soil and bank erosion, under field drainage and sediments from joining tributaries, whereas diffuse (eroded soil) and point (STW's, field drains) sources are the likely principal sources of P. Subsequent variations in local geomorphology, natural disturbance regimes (e.g. in-flowing tributaries) and human interactions (e.g. land drainage, STW's) combine to produce a continuum of in-stream sediment conditions with respect to the geochemistry and concentrations of P (Naiman et al., 2000; Fisher et al., 2004). Using a combined knowledge of catchment soil and river sediment geochemistry, an estimate of sediment P enrichment in the Nene, compared to the catchment soils, was made. Results demonstrated that there was little difference in the geochemistry between the major soil parent materials. Recent source apportionment studies have suggested that channel banks and under-field drainage are the greatest contributors to suspended sediment, followed by topsoil and road drainage (Cooper et al. 2015). It was observed during sample collection in the current study that under-field drainage was an important source of sediment into the river along the distance sampled. However, evidence from the sediment PSD analysis and field observations suggests that much of the clay fraction will stay suspended and be washed through to the tidal part the river system. The P load released to the system by this lost sediment is not known. However, it is likely that if it is transported directly from the non-tidal river system it will have remained in oxygenated environments and if sorbed to Fe or Al oxides will remain so, unless utilised by microbes or biota. However, if it is trapped and buried within sediments it may contribute to the P enrichment found in the sediment, possibly undergoing changes in its redox status and being re-precipitated as a mineral phase such as vivianite. Thus considering that there generally is not a large fining of the sediment, no substantial increases in oxide surfaces and that the PSD of sediments is broadly similar to the soils, it is likely that a considerable part of the P enrichment particularly in water bodies 4–6 is derived from in-stream sorption of SRP released from the STW's within the catchment. In the more urban influenced part of the catchment (water bodies 4–6), this enrichment might have caused at least a doubling of P_{Total} compared to typical soil concentrations found within the catchment. This estimate was based on a reasonably recent geochemical survey of the catchment soils and although P concentrations may have declined slightly in the soils (particularly in terms of P_{Labile}) since the geochemical survey was undertaken through improved P fertiliser management, in water bodies 4–6, a substantial shift in the shape of the sediment CDF compared to catchment soils for P was found.

Once sorbed, the key question is whether and how this sediment P is fixed in non-labile forms and how easily it may be released. Where anaerobic conditions have developed within the sediments, mineral phases such as vivianite, or the inclusion of P as a minor constituent of other minerals (e.g. $MnCO_3$), represent forms of P fixation and were identified. However, most P is sequestered, particularly in the lower waterbodies within the oxalate extractable Fe, Al and Mn. For example, by water body 6 up to 90% of P_{Total} was associated with the oxalate extractable (mainly amorphous oxides) compared to 31% in water body 1. This was possibly due to the deeper sediments in the lower water bodies and changes in redox status and P speciation. Agudelo et al. (2011) found a similar response and suggested that increases in P associated with amorphous oxides was a result of increased sediment depth changes in redox status and a fining of the particles size as distance from the headwaters increased. Concentration gradients of oxygen with increasing depth in sediment will determine the magnitude of oxidation and oxide speciation. Typically, FeOOH is associated with phosphate sorption in sediments, particularly within the upper oxygenated sections (e.g. 0–10 cm) (Agudelo et al., 2011). Our laboratory measurements of K_r, determined in oxygenated conditions demonstrate the importance of FeOOH and AlOOH. However, within the sediment, there will be a mixture of aerobic–anaerobic zones in the sediments. Oxygen egress from the roots of macrophytes and benthic micro-algae can help form oxides and several studies have demonstrated increased P fixation under macrophyte roots (Jaynes and Carpenter, 1986; Christensen, 1997; Christensen et al., 1997).

Sediment geochemical properties (e.g. redox change as evidenced by the formation of minerals such as vivianite, clays, oxides) throughout the river length were also shown to determine sediment-water P interactions and the properties (labile P, EPC_0, K_r) that are most likely to influence the 'Ecological Status' of the river ecosystem. The concentration of P_{Labile} was typically <2% of P_{Total}. Concentrations of P_{Labile} in the sediment were found to be as large as 100 mg kg^{-1}, a value considerably larger than recommended for most agricultural soils. There was no correlation found between P_{Labile} and EPC_0, suggesting that the EPC_0 is buffered primarily by the part of P_{Labile} that is most weakly held and rapidly exchangeable. Isotopic exchange experiments using ^{32}P have demonstrated that parts of P_{Labile} can exchange very rapidly or over longer time periods. Thus P_{Labile} sorbed on different mineral or organic phases may respond at different rates to maintain solid $\leftrightarrow$ solution equilibria (Furumai et al., 1989). Results demonstrated that values of EPC_0 generally increased but only by a small amount between water bodies 1–3 and water bodies 4–6. Whilst small variations in EPC_0 may occur throughout each water body with time as river conditions and sediment particle size distribution change (Stutter and Lumsdon, 2008), the largest increases in EPC_0 are expected where there is a substantial increase in P_{Labile} as demonstrated in soils (Withers et al., 2009; Hartikainen, 1991). This is most likely to occur downstream of STW's (Jarvie et al., 2006). In the Nene, the EPC_0 was found to increase slightly where there was a general increase in P_{Labile}. Various interactions may occur that may change whether the sediment becomes a source or sink of P, with those sediments close to the EPC_0 and SRP equilibrium being most at risk. Release of P will occur when $EPC_0 > SRP$ and these conditions can be bought about by (i) the introduction of tertiary P stripping decreasing SRP concentrations downstream of STW's (Jarvie et al., 2006), (ii) the uptake of SRP by biota during summer periods, (iii) changes in texture bought about by changes in river velocity (House and Warwick, 1999) and (vi) the creation of anaerobic conditions through effluent discharge that may aid the release of P, causing eutrophication and decreasing SRP values. Concentrations of SRP in the Nene are of the order of ~6.45 μm P L^{-1} (0.2 mg P L^{-1}), having decreased as a result of the introduction of P-stripping in STW's, from 2 to 3 mg L^{-1} in 1998. Thus, with EPC_0 data in this study of 0.61–1.69 μm L^{-1} P it is likely that SRP will generally exceed EPC_0 under current conditions.

Whilst inorganic P species HPO_4^- and $H_2PO_4^-$ are the species of P used by macrophytes, the potential presence of organic P species (monoester P, diester P, Phytic-like P) in the sediments (not measured) will contribute to P_{Labile} as P is released from organic P species through enzymatic hydrolysis to inorganic P (Wang and Pant, 2010; Zhu et al., 2013). Thus a consequence of large concentrations of bioavailable P in river sediments is that macrophyte and algal growth are likely to increase. The availability of P and sediment deposition can be closely linked, particularly in relatively slow flowing rivers like the Nene. Rooted aquatic plants have the potential to derive almost all their P requirements from bioavailable sediment P reserves (Mainstone and Parr, 2002), although Pelton et al. (1998) suggested that the relative contribution of root uptake to macrophyte P demand varied on the SRP concentration in the overlying water. The increased growth of aquatic plants can lead to increased trapping of sediment. Mainstone and Parr (2002) suggest that high concentrations of labile P can (i) increases re-growth after plant management, (ii) alter the species community structure, favouring species with high growth rates and (iii) reduce root depth, potentially increasing the plants susceptibility to being detached at high river flows and associated sediment remobilization (see section 3.1).

An important issue raised by this work and which is poorly understood but which is essential to sediment-P interactions within river systems is sediment residence time, of which little has been published. After undertaking the sampling on the Nene it was apparent that extended periods of high water flow can remove significant areas of macrophyte communities, along with the sediment that the roots hold in place and the P associated with it. This is a recognised occurrence for the River Nene (Brierley et al., 1989), but may play a vital role in the self-cleaning of the river of legacy P. Thus the sediment remaining in place after these periods of flooding and high flow demonstrate the importance of sediment position, particularly with respect to being protected from rapid river flow. Thus this may lead to possible longer residence times. Therefore more work is required to understand to what extent flooding and high water flow may desilt rivers such as the Nene, and in particular the size and duration of flooding that causes significant desilting to occur. The evidence from this investigation also suggestions that the rate of sediment build up and the associated temporal changes in sediment-P interactions also require further understanding.

In the current work the concentration of MnO_x was identified as a key predictor in the various species of sediment P modelled, particularly in predicting P_{Total} and P_{Labile}. This is despite the significantly lower concentrations of MnO_x compared to FeO_x limiting the contribution that MnO_x can make to the binding of P (Bortleson, 1974; Christensen et al., 1997). It is also generally recognised, that despite its large surface area, its surface chemistry (negative surface charge at near neutral pH) is less suitable for P sorption than that of Fe oxides (Kawashima et al., 1986; Tipping et al., 1984; Yao and Millero, 1996). In addition, changes in the oxidation state of MnO_x may limit its ability to sorb P as Mn^{2+} oxyhydroxides have greater sorption capacity than the Mn^{4+} oxyhydroxides which form quickly with exposure to air (Lu and Liao, 1997). Bortleson (1974), who also found strong positive correlations between Mn_{Ox} and P in sediments, suggested that the supply rate and migration of Fe and Mn as influenced by pH and redox conditions caused the iron concentrations, more than the Mn concentrations to vary independently of the final P concentration. Thus the suggestion is that within the $Fe_{Oxalate}$ or Fe_{Total} pools, alongside FeOOH there exists a range of poorly crystalline $Fe^{(II)}$ or mixed $Fe^{(II)}/Fe^{(III)}$ minerals that have different P binding properties. These may include $Fe^{(II)}(OH)_2$ or green rust (a precursor to vivianite) and magnetite (Boughriet et al., 1997). In addition, Crosby et al. (1981) suggested that large differences in P sorption characteristics exist between Fe^{2+} and Fe^{3+} derived FeOOH under natural conditions. This difference is a result of the different structures of FeOOH formed from either ferric or ferrous iron as well as their ageing properties.

Thus, the strong predictive power of MnO_x in the models presented in this paper, combined with the knowledge that FeOOH is the more effective P binding surface suggests that, particularly in sediment aerobic–anaerobic transition zones present in the homogenised cores, mechanisms may exist that link the two oxides in the fixation of P. In aquatic aerobic–anaerobic transition environments, MnO_x has been identified as playing a fundamental role in the process through which Fe^{2+} precipitates to form FeOOH or in the co-precipitation of Mn/Fe oxy-hydroxides (MnO_x–FeOOH) on which P is later sorbed (Dellwig et al., 2010; Hongve, 1997). Zhang et al. (2009) and Lu et al. (2014) have both reported that mixed Fe–Mn binary oxides are highly effective at sorbing P. The formation of these MnO_x–FeOOH phases have been identified in particle analysis from the redox transition zones of ocean waters, where P adsorption forms part of tight element cycling involving Mn–Fe-P (Dellwig et al., 2010). Formation occurs when biogenically produced MnO_x (Tebo et al., 2004), oxidises Fe^{2+} and Mn(IV) ions are replaced by Fe(III) ions. Postma (1985) suggested that the Fe^{3+} released in this reaction will most likely precipitate as FeOOH on the surface of the MnO_x particle. This can be followed by immediate adsorption or co-precipitation of P. Van der Zee et al. (2005) suggest that the oxidation of Fe^{2+} by MnO_x may be more common than realised but may not be obvious where there is significant NO_3^-. Mixed MnO_x–FeOOH-PO_4 oxides in the Nene sediments were identified with both SEM and STEM analysis.

4. Conclusions

We examined the distribution of P_{Total} and P_{Labile} along a 100 km stretch of the non-tidal river Nene to understand how sediment-P may contribute to river SRP concentrations. Key points identified for sediment management within the Nene Catchment are (i) that the accumulation of sediments generally increases with distance from the headwaters, (ii) the extent of P enrichment appears to be largely influenced by the transition from a rural to a more urbanised catchment where there are increasing population numbers along with larger and more frequent STW's and (iii) that fixation in oxalate extractable phases is a major pathway through which P is fixed within mineral phases. Whilst increases in P_{Labile} were found with distance from the headwaters concentrations were generally <2% of the P_{Total} and did not appear to be a directly related to EPC_0 concentration. This work also demonstrated that localised differences in particle size distribution influences P speciation within the broader trends of sediment and P accumulation.

However, the natural clearance of sediment during periods of high water flow, as was found in the sampling undertaken appears to be effective at removing much sediment from the non-tidal river channel, and further assessment of this natural process is needed. Further work should focus on the source of the sediment to the river, particularly in determining the proportions that enter the river via land drains, along with natural and cattle driven bank erosion, these possibly be the greatest sources. In addition, complete budgets of SRP and particulate associated P entering the river from land drains should be considered to assess contributions from these sources. Within this the role of buffer strips needs further investigation as these have been found to be a source of SRP (Stutter et al., 2009). Combining knowledge of the sediment and P budget along with greater understanding of sediment residence time is required to understand more fully the extent of in-stream sorption and release of P.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.apgeochem.2015.12.014.

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