DISTRIBUTION AND SPECIATION OF PHOSPHORUS IN FORESHORE SEDIMENTS OF THE THAMES ESTUARY, UK.

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Abstract

Estuarine sediments can be a source of Phosphorus (P) to coastal waters contributing to nutrient budgets and geochemical cycles. Whilst salt marsh sediments have been extensively studied, fewer studies have examined the potential P storage of foreshore or inter-tidal mud flat deposits. In this work, the concentration and speciation of P in 47 cores were examined from the inter-tidal mud flats of the tidal river Thames, from west London to the North Sea (~120 km). Results of P concentration and speciation were combined with published data relating to known sediment dynamics and water chemistry within the estuary to produce a conceptual model of sediment-P behaviour. Highest concentrations of total P (median concentration ~3000 mg kg^{-1}) were found close to the centre of London, probably as a result of inputs from major sewage treatment works. However, results showed that significant P desorption occurred after sediment passed through the Estuarine Turbidity Maximum and when the salinity of the river water exceeded ~6 ppt. In the outer estuary median total P concentrations fell to ~1000 mg kg^{-1}. Organic and inorganic species of Phosphorus were extracted and it was found that organic P was desorbed to a greater extent than inorganic P in the lower estuary. Models were developed to predict Total P (R^2=0.80), oxalate extractable P (R^2=0.80) and inorganic P (R^2=0.76) from sediment geochemical and river water properties. As the foreshore mud flats consist of deposited suspended sediment, concentrations of inorganic and organic P reflect largely the effects water chemistry has on P speciation and concentration. Thus suspended sediment, along with remobilised sediment from the upper estuary are likely to undergo similar desorption processes as they pass down the estuary.

Keywords: Estuary, London, Phosphorus, Speciation

1. Introduction

The transport of phosphorus from terrestrial to oceanic environments has important implications for the quality of fresh and marine waters (Eyre and Balls, 1999). The EU Water Framework Directive (Directive EC 2000/60/EC) was introduced to prevent further deterioration and improve the quality of inland surface waters whilst promoting ‘good ecological status’ (GES) with respect to biodiversity in rivers (Johnes et al. 2007; EA, 2014). In addition, the EU waste water Directive (Directive EU 91/271/EEC) aimed to reduce the amount of P released from Sewage Treatment Works. However, whilst statutory legislation for P concentrations in estuarine waters have yet to be introduced in the UK, improvements in the quality of river water leaving the catchment are likely to impact estuarine and marine systems as phosphorus is a key element contributing to eutrophication, algal and planktonic blooms (Correll, 1998; Davidson et al. 2014).

Whilst aquatic P species may dominate the nutrient cycle within estuarine systems, contributions to estuarine P budgets will also be derived from the P stored within the system, including sediments. Thus an initial stage to understanding the contribution sediment-P produces within estuarine waters is to obtain knowledge of the sediment distribution and movement, along with changes in sediment-P speciation within the tidal length of the river and estuarine system. The geology of the catchment controls important sediment properties such as texture and geochemistry whilst the catchment geomorphology influences river velocity and channel morphology which determines accumulation position, sediment depth, along with trapping systems such as macrophytes (House & Warwick, 1999) or man-made structures. In addition, the locations and type of P inputs (e.g. STWs and soil erosion) will determine inputs of P into the river or estuary. For example, recent work by Tye et al. (2016) on the non-tidal river Nene demonstrated an increase in sediment P concentrations with distance from the head waters, with point sources (STW’s) and the increasing urbanisation of the catchment being considered a major influence on the increasing P sediment concentration.

One area of P storage within estuaries which have received less attention than salt marsh sediments are foreshore or inter-tidal mudflats. Whereas, salt marsh sediments are considered relatively efficient sinks for nutrients (Coelho et al. 2004), fore-shore mudflats differ in that they are devoid of vegetation and undergo submersion twice a day. They represent a temporary storage zone, but like salt marsh sediments have the potential to supply the water column with P either through mineralisation or P desorption (Coelho et al. 2004; Mortimer et al. 1998; Wang and Li, 2010). Mudflats undergo cycles of deposition and erosion over differing timescales with their elevation and morphology controlled by tidal forcing and river discharge (Baugh et al. 2013). In addition, wind events and biological activity may complicate the deposition and erosion events (Deloffre et al. 2007). Phosphorus interactions with sediment in tidal sections of rivers are known to differ markedly from those in fresh water (House et al. 1998; Sundareshwar and Morris, 1999). This is largely through the role of increasing salinity and ionic strength that leads to the release of sediment bound P and flocculation of suspended sediments in the turbidity maximum (House et al. 1998). Phosphorus stored within these sediments can exist in many forms including inorganic P species, organic P species and in mineral phases such as calcium phosphate (apatite) or vivianite. Redox changes can either initiate the release or fixation of P from oxide phases (Reddy et al. 1995; House & Dension, 2000). Sulphate may also influence the release of P from Fe oxide phases leading to the recycling of sediment P (Caraco et al. 1989). The release of sediment P may be through the Equilibrium Phosphorus Concentration (EPC_0) model (Froelich, 1988). These processes may contribute to increasing P concentrations in estuarine waters and export to the oceans (Fox et al. 1986; Lebo and Sharp, 1992) where biological uptake and recycling are intensive, especially if N is not limited (Correll, 1998). This can lead to changes in the speciation of suspended sediment and particulate P which can be seasonally influenced (Zwolsman, 1994).

This paper investigates the controls on P concentration and speciation within the inter-tidal mudflats of the tidal River Thames, UK, a major UK river which flows through London. Recent work by Powers et al (2016) produced a history of P fluxes (Kt yr^{-1}) within the Thames catchment and demonstrated that between 1940 and 1980, inputs of P into the catchment in order of importance, were fertiliser P, food/feed export from farms, food waste to landfill and P input from sewage to treatment works. These were found to greatly exceed river export. However, since the late 1990's, and during the 2000's, gross annual exports from the landscape pool (land & river) of the Thames basin have slightly exceeded inputs. However, the results described by Powers et al. (2016) demonstrate how in the Anthropocene, the P cycle within catchments is dominated by human inputs which greatly exceed fluvial export and that substantial P is stored within components of the catchment. Whereas much work has been undertaken on the controls on P and improvements resulting from P stripping in STW's of the upper Thames catchment (Neal et al. 2000; Neal et al. 2010; Neal et al. 2006), this work examines the tidal section that flows through central London to the North Sea, and where significant P is released from some of the largest STW's in Europe. As the tidal mudflat sediments are formed through the sedimentation of suspended sediment, they present an archive of the environmental effects on suspended sediment P interactions and secondly on those processes when sediment P is in temporary storage within the mudflat. By combining data on the concentration and speciation of P with knowledge of the sediment transport system, a broad conceptual understanding of P cycling can be made for the tidal Thames.

2. Materials and Methods

2.1 Study area

The river Thames is the UK's longest river with a length of 345 km, a catchment area of 12935 km^2 and with an average discharge of 65.8 m^3 s^{-1} (Marsh and Hannaford, 2008). The rural upper catchment consists largely of agricultural land on limestone and chalk geology, flowing through a succession of large towns / small cities, before flowing through the centre of the city of London and out to the North Sea (Figure 1). The fore-shore mud flat sediments examined in this work are from the tidal section of the Thames which consists of a 120 km section from Teddington Lock in west London to the Essex coastline.

To understand the dynamics of P storage within these fore-shore sediments, understanding of (i) the origin of the sediments, (ii) their movement and (iii) inputs of P into the system is required. There are two main sources of sediment within the tidal river, these (i) originating from the catchment upstream of Teddington, and (ii) the tidal remobilisation of sediment in the estuary and transport upstream. Littlewood and Crossman (2003) provide an indication as to the extent that particles may travel. They suggest that if a particle started at Southend (Core 46; Fig 1) it may move upstream 12 km on a large spring tide and 17 km if the particle started at Greenwich (Core 14; Fig 1). However, suspended sediment would only drop out to form the mud-flats when current velocity and particle size are appropriate. Deposited sediment may erode when the critical threshold for re-mobilization is next achieved. The movement of sediment in suspension will be greatest on spring tides and least on neap tides, due to the greater forces produced by the spring tide. In addition to the suspended load, a great deal of sediment is transported upstream as near bed load where high concentrations and fluxes can occur. It would appear that this process is driven by salinity gradients and freshwater flow. Thus, in periods of low fresh water flow (April to September) the average salinity in the Blackwall Point and Lower Gravesend reach increases as it does not undergo as much dilution from the fluvial flow. This seasonal salinity change results in sediment being moved upstream and deposition occurring, where the salinity and flow velocity are suitable. This is a slow process and takes several months. In autumn, the increased fresh water flow may re-mobilise cohesive bed sediments. Results suggest that most of this sediment moves at very high concentration in the deepest parts of the channel, with only a small part of the sediment rising into suspension. However, within a few days this downward channel movement of sediment can reverse the whole of the summer period upstream transport.

We have divided the tidal Thames into four zones based on suspended sediment concentrations by Littlewood and Crossman (2003). Zone 1 stretches from Teddington Lock to Lower Pool (Cores 1-12) and in this stretch the suspended sediment concentrations are generally low with concentrations at Putney (17 km from Teddington of 40-120 mg L^{-1} and at Vauxhall Bridge (27 km from Teddington Lock) of 60-140 mg L^{-1}. Within this zone there is little deposition of sediment on the banks of the river with much of the sediment passing through. Zone 2 (Cores 13-27) covers the distance between Lower Pool to Erith Reach (24 km) and includes the turbidity maximum around Gallions, Barking and Halfway reaches (Cores 17-27). Traditionally these are known as the ‘mud reaches’ as this is the limit of saline intrusion which causes flocculation and deposition of the sediment. The position of the turbidity maximum is liable to fluctuate with tidal range, sea level changes and the seasonal change in freshwater and saline tidal flow. The movement of this saline front has a fundamental effect on the deposition of sediment. During winter, when river flow is high, the saline water front is pushed back and this causes the sediment to be flushed out of the ‘Mud Reaches’ and stored in the Gravesend Reach area of Zone 3 (Cores 30-32). In the summer when river flow is lower the saline front moves back upstream, which again starts the process of flocculation and deposition of the sediments. The suspended sediment concentrations are highest in this zone with concentrations at Barking in the range 500-600 mg kg^{-1}. Zone 3 (Cores 28-33) occupies the distance from Erith to Lower Gravesend Reach (20 km) and generally has moderately high suspended sediment concentrations with concentrations at Tilbury between 200-400 mg L^{-1}. Zone 4 (Cores 34-47) is the area between Gravesend to Sea Reach spans a distance of 27 km and connects the estuary to southern North Sea. Combined with these general sediment dynamics are inputs of dissolved and particulate P. In Zone 1, P inputs will be from the agriculture and STW's sited in the upstream catchment. Within Zone 1 there are additional major inputs from the STW at Mogden. In Zone 2, there are three major STW's including those at Becton, Crossness and Riverside, whilst in Zone 3 there is the Long Reach STW. In addition, to P discharges from all these STW's sewage is discharged into the Thames via overflow sewers during times of heavy rainfall.

2.2 Sediment Sampling

Two sets of sediment were collected, (i) sediment cores (n=47) collected in non-sequential order in November 2009, October 2010 and November 2011 from zones 1-4 and (ii) a further 23 surface grab samples (2-5cm deep), representing the most recently deposited sediments and were collected using a stainless steel trowel from zones 1 and 2 in November 2011. Sample positions of cores (C) and surface grab samples (G) are shown in Figures 1 and 2 respectively.

Inter-tidal sampling sites were accessed by Port of London Authority Dory attached to the vessel Driftwood II, using pre-determined GPS co-ordinates (Vane *et al*., 2015). At each core site, clear polycarbonate tubes (140 cm length × 6 cm I.D) fitted with a stainless steel basket catcher at the base were manually driven into the exposed sediment and extracted to recover the core material (Vane *et al*., 2011; Vane *et al*. 2007). Sediments were frozen at -18° C within 3 h of exhumation and transported frozen in the dark from London to the BGS laboratories to avoid post-collection chemical changes and physical movement. Upon receipt each core was cut longitudinally in half and sliced into 10 cm intervals (Vane *et al*., 2013). The resultant sediment samples were freeze-dried, disaggregated, sieved to pass a 2 mm mesh. A subsample of the < 2mm fraction was ground to a fine powder using an agate ball-mill (Beriro *et al*. 2014). Prepared Thames sediments were subsequently stored in the dark at 14°C in sealed polyethylene bags. All samples were thoroughly mixed to avoid inhomogeneity caused by density settling during storage.

2.3 Analytical Methods

Total element concentrations in the sediment cores were determined using XRFS Spectrometer using the same analytical method, instrumentation and calibration package as previously reported for mangrove sediments (Vane *et al*., 2009). TOC was determined using a Europa Scientific Elemental Analyser, after samples were treated with 1M HCl, and washed with deionised water to remove inorganic C, before being oven dried at 60°C (Lopes dos Santos and Vane, 2016). Estimates of poorly crystalline oxyhydroxides of Fe (FeOOH), Mn (MnO_x) and Al (AlOOH) in sediment were determined using 0.2M ammonium oxalate and 0.125M oxalic acid extractions. Samples were shaken in darkness for 2 hours (McKeague & Day, 1966), centrifuged at 3500 rpm and filtered (0.45µm nylon syringe filters) before analysis by ICP-AES. Using results from the oxalate extraction the Degree Phosphrous

Saturation (% DPS) can be estimated as $P_{Oxalate}/(Fe_{Oxalate} + Al_{Oxalate})*100$. Estimates of Total Organic Phosphorus were made by extracting samples using 0.25M NaOH and 0.05M EDTA for 16 hours at 20°C (Turner et al. 2003). After extraction sub-samples were analysed for (i) 'Inorganic P (molybdate reactive P)' ($P_{Inorganic}$) and (ii) total P with estimates of organic P

($P_{Organic}$) being the difference between the two measurements. $P_{Inorganic}$ was measured by molybdate blue immediately after extraction and Total P in the extracts was measured by ICP-AES. Methodological constraints have been discussed in previous work (Worsfield et al., 2008). It is possible that the within $P_{Inorganic}$ measurement some acid hydrolysable organic and condensed P may be included through the molybdate blue analysis and within $P_{Organic}$ measurement some inorganic polyphosphates may be measured (Turner et al. 2003). Samples were analysed in batches of 30, with two samples selected that were extracted and analysed in every batch. These were samples core 41 (20-30 cm) and core 35 (10-20 cm). For the $P_{Inorganic}$ measurement the nine replicates from core 41 gave a mean concentration of 448 mg kg^{-1} ± SD = 16.36 (% CV = 3.64; n=9) and for core sample 35 a mean concentration of 805 mg kg^{-1} ± SD = 38.88 (% CV 4.83, n=9). For the ICP-AES measurement of Total P in NaOH solutions, the core 41 sample gave a mean concentration of 495.6 mg kg^{-1} ± SD 23.1 (% CV = 4.66 %; n=9) and core sample 35 gave a mean concentration of 878.2 mg kg^{-1} ± SD 17.28 (% CV = 1.97; n=9). In some samples $P_{Inorganic}$ was found to be equal or slightly greater than the ICP-AES measurement thereby returning a negative $P_{Organic}$ value. This is probably associated with experimental (e.g. Worsfield et al, 2008) and analytical error associated with each method. Therefore an ‘uncertainty propagation’ analysis was undertaken for samples, using information obtained from the replicates samples and based on 95 % Confidence Intervals to ascertain samples which had a robust and identifiable $P_{Organic}$ concentration. Results suggested that those $P_{Organic}$ concentrations < 21 mg kg^{-1} were not sufficiently robust and were therefore not included within the dataset.

Scanning electron microscopy (SEM) was undertaken to characterise the sediments and identify P containing mineral phases. Sub samples of sediment were mounted on stubs and were coated with a thin film of carbon approximately 25 nm thick using an EMITECH 960L evaporation-coating unit. Analyses were performed using a LEO 435VP variable pressure SEM, and an FEI Quanta 600 environmental SEM, under high vacuum (<1x10-4 Torr) and variable vacuum (0.45 Torr water atmosphere) conditions respectively. Accelerating voltages of 20kV were used in both. SEM photomicrographs were obtained under backscatter electron imaging (BSEM) and secondary electron imaging (SE) conditions as 8 bit greyscale TIF format digital images. Phase/mineral identification was aided by qualitative observation of energy-dispersive X-ray spectra recorded simultaneously during SEM analysis, using Oxford Instruments INCA energy-dispersive X-ray microanalysis (EDXA) systems. One core from each of the 4 sediment zones of the tidal Thames were selected and three depths analysed, these being:

Zone 1 – Core TH29, 10-20 cm, 30-40 cm and 60-70cm

Zone 2 – Core THS3, 0-10 cm, 30-40 cm and 50 -60 cm

Zone 3 – Core TH10, 10-20 cm, 40-50 cm and 70-80 cm

Zone 4 – Core TH2, depths 10-20 cm, 30-40 cm 50 – 60 cm

3. Results and Discussion

3.1 Sediment characteristics

It is important to assess the geochemical characteristics of the sediment prior to examining changes in the P concentrations and speciation. This is to ensure that a change of sediment source is not responsible for the changes in P properties. For example, it has been suggested that the Thames estuary may receive sediment from sources such as the North Norfolk coast where extensive cliff erosion occurs. Total mean concentrations of Al and Si for each core were determined from the 10 cm sections, and used as proxies of alumina-silicate minerals, so that geochemical relationships of the sediment between the inner and outer estuary zones could be examined. Results showed that there was reasonable consistency in Si and Al concentrations, along the length of the Thames estuary (Figures 3a & 3b). There was possibly greater variation in Zone 1 cores closer to Teddington Lock, possibly because of less tidal mixing further up the river. A further test to assess changes in sediment source was to examine the relationship between Al and Rb, with the hypothesis that clay minerals derived from different sources would have different Al:Rb ratios (assuming that a significant proportion of the Al present was as clay minerals and that Rb is largely present in the clay minerals). Figure 3 shows a very strong correlation (r^2 = 0.95) between Al and Rb for the whole dataset, suggesting that the sediment is likely from a similar source or is well mixed within the estuary before sedimentation. Similarly strong correlations were found between other clay components including K v Ti (R^2=0.92), Ti v Al (R^2 =0.97) and Ti v Mg (R^2 =0.89). There appeared to be no definite trend in sediment depth throughout the estuary although depths varied from 10 cm to >1m (Figure 4a).

3.2 Total Phosphorus in foreshore sediments

Results from the sediment geochemical analysis suggest that (i) the sediment collected from the fore-shore appeared to be from one source (or thoroughly mixed) and that there was not a distinctive fining of the sediment towards the estuary mouth. Both of these factors could influence P_{Total} distribution, but based on these results it does not appear that they have a large influence. Using the sediment zone classification of Littlewood and Crossman (2003) and described in the Material and Methods, mean P_{Total} concentration in each core was determined by averaging the 10 cm depth increments. These were then plotted against their distance from Teddington Lock (Figure 4c). It is evident that mean P_{Total} concentrations were highest in Zones 1 and 2 with a large fall in concentrations in Zone 3 and 4. When compared to the salinity concentrations transect (Figure 4b) taken from the data of Pope and Langston

(2011), it can be seen that the decrease in P_{Total} concentrations in Zones 3 & 4, occurs when there is an increase in salinity above ~6 ppt.

Figure 5 shows the variation of P_{Total} concentrations within the 0-10 cm sections from cores from each of the 4 sediment zones using Box and Whisker plots, along with the grab samples taken from Zones 1 and 2. The greatest variation and range of P_{Total} concentrations were found in Zone 1, possibly because there is less mixing of sediment towards the tidal limit (Teddington Lock). For Zone 2, the range of P_{Total} concentrations was smaller than in Zone 1 and the P_{Total} concentrations between the 25th – 75th percentiles showed less variation than in Zone 1. For Zones 3 and 4, it was evident that the concentration ranges of P were greatly reduced compared to Zones 1 and 2, and with less variation, particularly between the 25th and 75th percentiles. Median values for the grab samples from Zone 1 and 2 were higher than the mean P_{Total} concentrations in the cores taken from their respective zones, but the distribution of concentrations were broadly similar. Thus the grab samples did not demonstrate that the P_{Total} concentrations in the most recently deposited sediments were significantly different from the core sample concentrations. The reasonably consistent concentrations of P_{Total} within the 25th to 75th percentiles ranges in the cores from each zone probably reflects the (i) thorough sediment mixing due to the strong? tidal cycle (see Section 2.1), storm events and anthropogenic physical disturbance (e.g. maintenance dredging) and (ii) the controls that water properties (e.g. salinity) may produce.

The relationships between P_{Total} and the elements it is likely to form mineral phases with or act as a binding surface with were examined. Initial exploration of the data (n=279 samples) identified a series of outliers which prevented models involving P_{Total} to parameterise effectively. These outliers were removed from the dataset, prior to further P_{Total} data analysis. Core 29 (Rainham) values were removed as this core came from was a salt marsh sample, rather than a foreshore mudflat sediment, and because its environmental setting led it to have very different geochemical properties. There were also a series of samples (n=20) where Fe_{Total} concentrations were > 60 000 mg kg^{-1}. The values removed came largely from core 32 (Shorne, n=5), core 24 (Crossness, n=4), core 33 (Cliffe, n=2), core 25 (Dagenham Ford Pier, n=3), and core 28 (Dartford, n=3) with individual values coming from 2 (Chiswick Bridge), 13 (Deptford Creek) and 10 (Vauxhall Bridge). These samples also had elevated concentrations of trace metals, compared to the remaining dataset. For Cores 24, 25, 32 and 33 these included V and Co suggesting that the higher concentrations of Fe in these samples may have been derived from metallurgical industries.

After removing these 20 samples, reasonably strong relationships between P and TOC (r=0.77) and Mn (r=0.76) with P_{Total} were found (Figure 6). Generally, poor relationships were found between Fe_{Total}, Al_{Total} and Ca_{Total} and P_{Total}. To further understand the geochemical associations of P, SEM analysis of selected cores samples (Section 2.3) were undertaken. All samples analysed contained mainly silicates, with some Ca carbonates (mostly as coccoliths) and iron-titanium phases (ilmenite) being present. However, the mineral phase which was ubiquitous was pyrite (FeS_2) suggesting the presence of reducing conditions throughout the cores examined from the four different zones (Figure 7). Minerals containing P were rare in all the samples examined. However, occasional P containing minerals were found. For example, in core 2 (Zone 1) at a depth of 30-40 cm, a small fragment of apatite included within a mica (biotite) sheet was found. In core 26 (Zone 2), at a depth of 0-10 cm there was an altered Fe mineral, with a small concentration of P present, along with some infrequent apatite. At a depth 50-60 cm a rare-earth phosphate-mineral was found (aluminium-strontium–phosphate + rare earths). At a depth of 40-50 cm, a particle of amorphous Fe oxide containing very small concentrations of Mn and P was found. Possible vivianite (dominant detectable elements are Fe, P and O, with lesser Mn) was recognised in core 36 (Zone 4), at depths of 10-20 cm and 30-40 cm.

A regression model to determine the key variables that may explain the concentration of P_{Total} in the dataset (n=224) was parameterised. The best fit model for predicting P_{Total} had an adjusted R^2 of 0.80 and is presented in Table 1, with the observed v predicted values shown in Figure 8. The three significant ($P<0.001$) co-variables of the model were Mn_{Total}, TOC and salinity. It is likely that Mn_{Total} was significant as it is likely linked to the Fe(III) oxy-hydroxides that are involved in P adsorption and the positive relationship with TOC was likely because much of the P is released from STW's or sewerage overflow which also are likely to release organic matter. Salinity is included because of the role increasing anion (e.g. sulphate) concentrations may have on desorption of P species from the sediment (Caraco et al. 1989).

3.3 Oxalate Extractable P and non-crystalline oxides

All core samples and grab samples were analysed for $P_{Oxalate}$, an estimate of the P associated with the non-crystalline oxides of $Al_{Oxalate}$, $Fe_{Oxalate}$ and $Mn_{Oxalate}$, either being surface bound or fixed within the poorly crystalline oxide structure. Measurements are also likely to include P associated with the release of organic species, originally bound to the non-crystalline oxide phases (Basile-Doelsch et al., 2015). The relationships between Total Fe, Al and Mn and their oxalate extractable oxide phases (Figure 9) show that for $Fe_{Oxalate}$ and $Al_{Oxalate}$ the effects of salinity are apparent; there being a higher proportion of $Fe_{Oxalate}$ and $Al_{Oxalate}$ in sediment

Zones 1 and 2, than in Zones 3 and 4 where salinity is increasing, whilst the range of Fe_{Total} and Al_{Total} are broadly similar. For $Fe_{Oxalate}$ this may suggest that the increasing sulphate concentrations associated with salinity is producing FeS_2 (Caraco et al., 1989). For $Mn_{Oxalate}$, a linear relationship ($R^2 = 0.87$) was found with Mn_{Total} for the entire dataset.

Data showed that $P_{Oxalate}$ concentrations were broadly similar in pattern to P_{Total} with distance from Teddington Lock. Figure 10 shows the relationship between P_{Total} v $P_{Oxalate}$ and demonstrates that for many samples the oxalate extraction removes a significant proportion of P_{Total}, with an overall relationship being:

$$P_{Oxalate} = 0.9765*P_{Total} - 347.2; \qquad R^2 = 0.88 \qquad \text{eqn. 1}$$

It was found that $P_{Oxalate}$ slightly exceeded P_{Total} in a small number of samples with the highest P_{Total} concentrations, these being from Zone 2 where the major STW's are sited. This is likely to occur when $P_{Oxalate}$ accounts for most of the P present along with any analytical error associated with ICP-AES measurements. The $P_{Oxalate}$:P_{Total} ratios found in the different sediment zones of the Thames was explored. A higher proportion of P was oxalate extractable in Zones 1 and 2 than in Zones 3 and 4 (Figure 11). Median $P_{Oxalate}$:P_{Total} in zones 1 and 2 was ~0.8 whilst in Zones 3 and 4 median values ~0.6. In addition, it was also obvious that those samples in Zones 3 and 4 generally had a more constrained distribution around the median value than samples in Zones 1 and 2. The suggestion from these results is that samples from Zones 1 and 2 have a lot of surface adsorbed P, possibly as a result of discharges from the STW's present but in Zones 3 and 4, this has been desorbed because of the increase in salinity. Correlations between $P_{Oxalate}$ and the non-crystalline oxides were assessed for the whole dataset (Figure 12). There were strong correlations between $Fe_{Oxalate}$ (r=0.89) and $Mn_{Oxalate}$ (r=0.79) and $P_{Oxalate}$, with a lesser correlation with $Al_{Oxalate}$. In addition, $\text{Mn}_{\text{Oxalate}}$ and $\text{Fe}_{\text{Oxalate}}$ showed a strong correlation (r=0.80).

The degree of phosphorous saturation (DPS) was examined to assess whether the decrease in the proportion of non-crystalline oxide surfaces found in Zones 3 and 4 are likely to be a constraint on phosphate sorption. In Figure 13, box and whisker plots show the % DSP for core samples in each zone and also from the grab samples taken from Zones 1 and 2. There was generally a lower % DPS in Zones 3 and 4 than in Zones 1 and 2. Median values of % DPS in Zones 1 and 2 were between 20 -30 %, whilst for Zones 3 and 4 they were between 10-15 %, suggesting that there is potential for further sorption in all zones.

A model to predict the concentration of $P_{Oxalate}$ was parameterised and results can be seen in Table 2 and Figure 14. In parameterising the model, the possible effects of salinity were considered as it is likely responsible for both desorption of phosphate species and also the lower proportion of non-crystalline oxides of Fe an Al that phosphates may bind too. Analysis of data showed weak negative correlations between salinity and $Fe_{Oxalate}$ (r=-0.35) and $Al_{Oxalate}$ (r=-0.51), suggesting that some interactions were present. Therefore, whilst a predictive model can be parametrised this small cross-correlation means that a comparison of the coefficients and their relative importance cannot be undertaken. Two models were parameterised, firstly one using the three oxalate oxide phases (Fe, Mn, Al) which had an adjusted R^2 of 0.75 and a second, where salinity was included with an R^2 of 0.80. Undertaking an ANOVA to compare the two model outputs it was found that the second model with salinity included was significantly (P<0.001) improved and is the one presented in Table 2 and Figure 14.

3.4 Estimates of NaOH extractable inorganic and organic P

Whereas the estimates of $P_{Oxalate}$ include inorganic and organic P associated with amorphous or non-crystalline oxides, improved estimates of inorganic and organic species were examined using the P_{NaOH} extraction. Concentrations of $NaOH_{Total}$ were related to P_{Total} and $P_{Oxalate}$ through the following equations:

$$\text{Total NaOH P} = 0.7208 * P_{Total};\ R^2=0.91 \qquad \text{eqn. 2}$$

$$\text{Total NaOH P} = 0.8060 * P_{Oxalate};\ R^2 = 0.94 \qquad \text{eqn. 3}$$

The equations demonstrate that the combined $P_{Inorganic}$ and $P_{Organic}$ fractions extracted using NaOH represent significant proportions of both the P_{Total} and $P_{Oxalate}$ pools. A general pattern existed for the NaOH extractable Inorganic and Organic P pools in that when $P_{Inorganic}$ was typically < 1000 mg kg^{-1}, the concentrations of $P_{Organic}$ were generally also low or below analytical detection. Thereafter as $P_{Inorganic}$ increases there was a concomitant increase in $P_{Organic}$ concentrations which often exceed the $P_{Inorganic}$, concentration. Figure 15 shows how concentrations of both $P_{Inorganic}$ and $P_{Organic}$ vary with distance from Teddington Lock, at three depth intervals; these being 0-10 cm, 30-40 cm and 50-60 cm. Missing values indicate that sediment was not present at that depth. Two trends can be seen in the data. Firstly, in zones 1 and 2, concentrations of $P_{Organic}$ were generally a higher proportion of the P extracted with NaOH than in zones 3 and 4 at all three depths, with the exception of TH7 which was the core taken on the salt marsh. The second trend shows that a substantial concentration of $P_{Organic}$ in zones 1 and 2 remains with increasing depth. In a similar manner to the $P_{Oxalate}$ model, two models were parameterised, one without salinity and one where salinity was included, because of the possible effects of salinity on the oxide surfaces and desorption of P. Model one predicted $P_{Inorganic}$ using $Mn_{Oxalate}$ and $Fe_{Oxalate}$ and had a R^2 of 0.69. The inclusion of salinity to the above model increased the adjusted R^2 to 0.76 and is reported in Table 3 and Figure 16. An ANOVA comparing the two models showed that the second model was significantly (*P*<0.001) improved by including salinity.

Discussion

The inter-tidal mud flats of the River Thames represent a temporary storage component for sediment associated P within the estuarine system, but one which is vulnerable to remobilisation, with the potential for the release of P to estuarine waters. Thus evidence from the spatial distribution and speciation of P in the intertidal mud flat sediments of the River Thames combined with existing information regarding salinity and sediment movement can be combined to provide a conceptual understanding of sediment-P release to water and storage (Figure 17). The fore-shore sediments are formed from deposited suspended sediment and therefore concentrations and speciation of deposited sediment-P are likely to reflect (i) the interactions between suspended sediment and the estuarine / river aquatic environment at the point of deposition and (ii) in-situ processes once it has settled. Results for the Thames suggest that the P concentrations and speciation in the intertidal muds can be considered in the context of the four suspended sediment zones suggested by Littlewood and Crossman (2003). These sections all differ in P inputs and environmental gradients (salinity, SPM). Zones 1 & 2 have large inputs of P from 4 major London STW's (Mogden, Abbey Mills CSO, Beckton and Crossness) combined with P originating from the catchment above Teddington lock, whereas Zones 3 & 4 represent an increasingly saline environment. Zone 2 generally had the most samples with high concentrations of P in the 25-75th percentile range, probably as a result of the STW inputs. Previous work on these core samples have suggested that the highest concentrations of the biomarker crenarchaeol, an indicator of ammonia-oxidising Thaumarchaeota were found in this zone (Lopes dos Santos & Vane, 2016). This Archaea has been found in STW effluent (Kim et al. 2007). Thereafter the two dominant factors to be considered when accounting for the change in sediment P distribution and speciation through the tidal river system are (i) sediment source and transport and (ii) salinity.

With respect to sediment source, several authors (e.g. Inglis & Allen, 1957; WPRL, 1964) who undertook sediment budgets have suggested that inputs from the wider coastline, particularly from the decay of cliffs north of the Thames estuary, were needed to balance sediment budgets for the Thames estuary. However, recent work by Baugh et al. (2013), who undertook a fine sediment budget for the Thames, suggests that no large marine source of sediment is required to balance the sediment budget. This concurs with the initial assessment of sediment geochemical relationships undertaken in this work. Correlations (r=>0.95) were found for the whole dataset for the major elements K, Rb, Mg, Al, and Ti, which typically make up the clay fraction. In addition the statistical relationships for these elements were not found to be different when zones 1 and 2 and zones 3 and 4 were compared, indicating that the geochemistry of the sediment samples largely represent a single source of well mixed sediment present throughout the estuary. One aspect of estuarine sediment movement that may enhance sediment mixing is the sediment shuttle that operates between zones 2, 3 and 4 and which was identified by Ingliss & Allen (1957) who used ^{46}Sc to track the movement of sediment in the Thames. This mixing of sediment is likely one reason for the relatively consistent P_{Total} concentrations found in each sediment zone, particularly between the 25th and 75th percentiles. Having ascertained that a change in sediment source is not the likely cause for changes in sediment P concentrations, other processes can be examined. Two key mechanisms can be considered, these being the interactions between (i) salinity and suspended sediment P before deposition and (ii) P interactions with salinity within the deposited sediment.

Previous work (e.g. Upchurch et al. 1974; Fox et al. 1986; Jordan et al. 2008; Zhang and Huang, 2011) suggests that salinity is a key control in the distribution and speciation of P within a river-estuary system, especially within the turbidity maximum and as suspended sediment passes from fresh to saline water. Desorption of surface adsorbed sediment P has been found as salinity increases (Upchurch et al. 1974; Deborde et al. 2007; Lebo, 1991), largely through increased ionic strength and competition from other anions (e.g. OH^-, F^-, SO_4^- and $B(OH)_4^-$) for sorption sites (Froelich, 1988). For example, Deborde et al. (2007)

found a decrease in both organic and easily exchangeable inorganic P in suspended sediment along a salinity gradient in the Gironde estuary in France. Salinity also influences sediment P concentration and speciation within the mud flat deposits because of the role sulphide plays in releasing phosphate. This is via the dissolution of Fe-P complexes and the formation of FeS_2 minerals (Krom and Berner, 1980; Caraco et al. 1989; Jensen et al. 1995). In addition, once deposited as mudflat sediment P sorption or desorption will be dependent on the Equilibrium Phosphate Concentration (EPC_0). The EPC_0 determines the potential of P desorption or adsorption of deposited sediment in relation to the concentration of P in the river water. Zhang and Huang, (2011) demonstrated that only minor differences were found in EPC values with salinities varying between 2-9 ppt. However EPC increased thereafter as salinity increased.

Within the Thames estuary salinity had the greatest influence on the interactions between sediment-P and its environment especially as the % DPS demonstrated sufficient oxide surfaces for P sorption, even in zones 3 and 4 where there was a lower proportion of oxide surfaces. Evidence of the salinity gradient on P desorption was found to be significant within the models predicting P_{Total}, and $P_{Oxalate}$, and $P_{Inorganic}$. In particular, as salinity increases to 6 ppt at the beginning of Zone 3 major changes in the concentration and speciation of P in the Thames sediments occurs. A secondary influence on P desorption may also be produced by the concentration of Suspended Particulate Matter (SPM), which also changes with salinity. Deborde et al. (2007) demonstrated in laboratory experiments that the salinity at which P desorption occurs changed with suspended sediment concentrations. When suspended sediment concentrations were low (< 83 mg L^{-1} SS) desorption occurred in the salinity range 0-3 ppt whilst with higher suspended sediment concentrations (when = or > 500 mg L^{-1})

desorption occurred 0-15 ppt. Thus the suggestion is that at higher SPM concentrations, desorption of P may occur at a higher salinity.

Examining the interactions between salinity and SPM with respect to the Thames mudflat sediments, conditions for P desorption from the sediment can be estimated (Figure 17). For the Thames, Uncles and Mitchell (2011) suggest an average surface salinity in the Estuarine Turbidity Maximum (ETM) of ~3 ppt, with its average position being between the Millenium Dome and Woolwich Reach (between Cores 15 and 14; Zone 2). Various reports have been published for suspended sediment concentrations in the ETM of the Thames (e.g. Uncles and Mitchell, 2011). However, Baugh & Littlewood (2005) suggested tidally and width averaged ETM SPM concentrations of approx. 600 and 150 mg L^{-1} at spring and Neap tides respectively. After the turbidity maximum, salinity rises to 4 ppt in Zone 2. However, P desorption does not appear to occur in Zone 2, Thus the SPM concentrations in Zone 2 may be sufficient to reduce P desorption as suggested by Deborde et al. (2007), even though the salinity has increased beyond the 3 ppt suggested for water with low SPM concentrations. In the Thames, P desorption from sediment appears to occur at the interface between Zones 2 and 3 (Cores 27 and 28). Reported environmental conditions where this occurs based on data from Uncles and Mitchell (2011) and Pope and Langston (2011) are a surface water SPM decline to less than 50 mg L^{-1} and a salinity increase from 4 - 6 ppt. These figures are a reasonable approximation of those given by Deborde et al. (2007), but demonstrate how the interaction between SPM concentrations and salinity may determine conditions for P desorption. Importantly, Deborde (2007) also suggested that P desorption was irrespective of pre-existing P concentrations in saline waters. It is likely that desorption of P from the Thames SPM occurs in waters with mean annual P concentrations that far exceed the Water Framework Directive standard (< 120 ug L^{-1}) required for Good Ecological Status in fresh waters (lowland, high alkalinity) (Defra, 2014). In summer and autumn, seasonal mean concentrations of 1500 and 1800 µg L^{-1} have been reported in the Thames Tideway (Thames Water Utilities Ltd, 2011). In addition, the Cross Ness STW, one of the largest in Europe discharges into the Thames only 5 km upstream of Zone 3. Data extracted from the EA WIMS (http://environment.data.gov.uk/water-quality/view/download) database for 2015 provide measurements of orthophosphate concentrations from Hammersmith Bridge (Core 4) to the ocean. Data suggests the mean value for 2015 (n=6) is ~1 mg L^{-1} for Zones 1 and 2, with a drop in orthophosphate to 0.5 mg L^{-1} by the end of Zone 3 and a concentration of <0.1 mg L^{-1} in Zone 4. Thus the suggestion is that P desorption occurs in waters with P concentrations of between 0.5 – 1 mg L^{-1}.

The salinity gradient also appeared to influence P speciation. This was demonstrated by both the $P_{Oxalate}$ and P_{NaOH} results. Results demonstrated that although approximately 70 % of the P_{Total} was held as P_{NaOH} extractable species throughout the tidal Thames (Equation 2), the proportion of inorganic and organic species appeared to change with increasing distance from Teddington Lock. In Zones 1 and 2, a greater proportion of organic P was generally found compared to samples from Zones 3 and 4, where P appeared to be predominantly inorganic MRP. Organic P is likely to be surface adsorbed, but binds less strongly than inorganic MRP, leading to its likely preferential desorption in saline waters (Gardolinski et al., 2004; Ruttenberg & Sulak, 2011). The source of much of this $P_{Organic}$ is likely to be outputs from the STW’s in Zones 1 and 2. However, evidence from the different depths reported (Figure 13) suggest that organic P remained a significant proportion of NaOH extractable P, even at depths as deep as 70 cm in zones 1 and 2.

The presence of P at

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suggests that it has not been utilised by bacteria. In freshwater lakes Reitzel et al. (2007) found organic P species including orthophosphate monoesters and orthophosphate diesters including Teichoic acid and DNA-P to sediment depths of 40 cm, and dated to ~100 yrs old.

However, without further speciation of the organic P fraction using techniques such as ^{31}P NMR, it is not possible to speculate further on these sources and processes. Examination of the mineral phases using SEM analysis demonstrated the relative paucity of P containing mineral phases in each of the 4 zones, but particularly in zones 3 and 4. There was a general absence of identifiable Fe-Mn-P oxide minerals that have been identified in freshwater river systems (Tye et al. 2016), possibly suggesting that the absence of plant roots prevents the distribution of oxygen required within the sediment to create large mineral surfaces for P sorption (Christensen et al. 1997). In addition, no definite identification of Vivianite minerals were found, which are typical of reduced sediments in freshwater and act as a sink for P within the sediment. However, the ubiquitous presence of FeS_2 phases, suggest that Fe is precipitating as FeS_2 minerals in preference to Vivianite in this saline system (Caraco et al. 1980).

Modelling of P species demonstrates that the oxides of Fe, Mn and Al were important for sorption, and these probably exist as very fine oxides phases, as larger particles were generally not detected using SEM. For P_{Total} the best fit model identified Mn_{Total} and organic C as being significant predictors. This is likely because the Fe_{Total} pool will include all the FeS_2, along with various Fe(II) oxide minerals that have low affinities for P. Similarly, the Al_{Total} will include that Al associated with clay. Both Tye *et al.* (2016) and Bortleston (1974) found that when large datasets of sediment P were analysed, Mn_{Total} becomes a significant predictor in models, despite MnO_x generally having a much lower concentration as compared to FeO_x. This therefore is a limitation on the contribution that MnO_x can make to the binding of P (Bortleston, 1974; Christensen et al., 1997). However, for the $P_{Oxalate}$ model all the oxalate extractable phases measured ($Fe_{Oxalate}$, $Al_{Oxalate}$ and $Mn_{Oxalate}$) were significant predictors in the model. In addition, both $Mn_{Oxalate}$ and $Fe_{Oxalate}$ were highly correlated and were both significant in predicting $NaOH_{Inorganic}$. Whilst $Fe_{Oxalate}$ and $Al_{Oxalate}$ are recognised as surfaces to which P sorbs, the role of $Mn_{Oxalate}$ is less clear as despite its large surface area, its surface chemistry (negative surface charge at near neutral pH; Kawashima et al. 1986) is generally considered less suitable for P sorption than that of FeO_x. However Yao and Millero (1996) found MnO_x to be an important adsorbent of phosphate in seawater whilst Kawasima et al. (1986) suggested that phosphate is sorbed by MnO_x via the presence of divalent cations (Ba^{2+}, Ca^{2+}, Sr^{2+}, Mg^{2+}) or transition metals (Mn^{2+}, Co^{2+}, Ni^{2+}) in aquatic environments. However the strong predictive power of MnO_x found when examined in large datasets is despite the accepted knowledge that FeOOH is likely a far more effective P binding surface. However, particularly in aerobic-anaerobic transition zones of sediments there may be mechanisms that combine the two oxides in the fixation of P. One possibility is that in aerobic-anaerobic transition environments, MnO_x plays a fundamental role in the process through which Fe^{2+} precipitates to form FeOOH or the co-precipitation of Mn/Fe oxy-hydroxides (MnO_x-FeOOH) on which P is later sorbed. This process has 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). The mechanism involves biogenically produced MnO_x (Tebo et al., 2004) oxidising Fe^{2+} allowing Mn(IV) ions to be replaced by Fe(III) ions. Postma (1985) suggested that the Fe^{3+} produced will most likely precipitate as FeOOH on the surface of the MnO_x particle, followed by immediate adsorption or co-precipitation of P. Thus the suggestion is that one of the reasons MnO_x is identified as being a strong predictive variable in models is because of its link to the pool of FeOOH that is sorbing P. Whilst the $P_{Inorganic}$ was modelled throughout the tidal Thames, no modelling or correlations were found for $P_{Organic.}$

One question this study has not been able to answer relates to how long and how much sediment-P remains in temporary storage. Baugh et al. (2013) suggest that during the 20th century the Thames experienced both anthropogenic and natural change in the morphology of the mudflats. In the upper estuary (landward of London Bridge) it is considered that the mudflats have decreased in size due to the tidal channel becoming deeper and wider. However seaward of Barking, the lower estuary has deepened and narrowed leading to a gain in intertidal area. Thus the nature of these mudflats is liable to change over time, with P being stored in different areas of the river as the mudflats develop. When eroded, the material may then be re-deposited within the system. In particular, this is relevant to the deposits in Zones 1 and 2 because any remobilisation and transport downstream is likely to lead to the release of P to the water column as salinity increases in Zones 3 and 4. It is difficult to estimate the age of the samples taken from each individual mudflat because their position and hence deposition environment within the estuary is unique. However, work undertaken looking at the distribution of different pollutants may provide some insights into these questions. For example, Vane et al. (2015) examined Hg through the same core samples as used in this study and in many cores the Hg concentration peaks were found at depths > 30 cm. In their paper they suggested that much of the Hg may have come from the oil and coal burning power stations of London (e.g. Battersea) which closed more than ~40 years ago. Thus it is considered that at least some of the core samples represent an integration of sediment-P processes over many years.

5. Conclusions

The concentration and speciation of P associated with sediments from the foreshore or inter-tidal mud flats of the tidal river Thames were examined. Results demonstrated that both sediment concentration and speciation were largely determined by the position within the salinity gradient. Whilst representing a temporary store for P, considerable amounts of sediment associated P in zones 1 and 2 remained highly mobile, with the potential of being desorbed if re-suspended and transported to more saline waters. This would lead to potential increases in nutrient status in the outer estuary and contribute to biogeochemical processes. Whilst the behaviour of the inorganic P largely reflects the current state of knowledge with respect to sorption processes, further work exploring the speciation of the organic P species is required, particularly related to the length of time that organic P is stored within mud flat sediments and its utilisation with increasing sediment depth.

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Table 1: Output from observed v predicted regression model for P_{Total} sediments

Coefficient	Estimate	Std Error	t-value
Intercept	1.1946	0.1532	7.795
Log Mn (mg kg^{-1})	0.7457	0.0582	12.811
TOC (%)	0.0626	0.0079	7.842
Salinity (ppt)	-0.0061	0.0011	-5.240

Residual standard error: 0.1585 on 249 degrees of freedom
Multiple R-squared: 0.80, Adjusted R-squared: 0.80
F-statistic: 344 on 3 and 249 DF, *p*-value: < 2.2e-16

Table 2: Output for observed v predicted regression model for $P_{Oxalate}$ in
sediments

Coefficient	Estimate	Std Error	t-value	
Intercept	-0.339	0.273	-1.240	
Log Mn (mg kg^{-1})	0.437	0.058	7.495	<
Log Fe (mg kg^{-1})	0.381	0.057	6.592	<
Log Al (mg kg^{-1})	0.321	0.075	4.239	<
Salinity (ppt)	-0.011	0.001	-8.582	<

Residual standard error: 0.208 on 279 degrees of freedom
Multiple R-squared: 0.80, Adjusted R-squared: 0.80
F-statistic: 287.5 on 4 and 279 DF, *p*-value: < 2.2e-16

Table 3: Outputs for observed v predicted regression model for $P_{Inorganic}$ ext NaOH for the Thames sediments.

Coefficient	Estimate	Std Error	t-value
Intercept	0.4880	0.1915	2.548
Log $Mn_{Oxalate}$ (mg kg^{-1})	0.5048	0.0636	7.928
Log $Fe_{Oxalate}$ (mg kg^{-1})	0.3231	0.0640	5.042
Salinity	-0.0130	0.0014	-9.273

Residual standard error: 0.2123 on 260 degrees of freedom Multiple R-squared: 0.767, Adjusted R-squared: 0.7643 F-statistic: 285.3 on 3 and 260 DF, p-value: < 2.2e-16

Figure 1: Map of sampling sites for core samples taken from the tidal River Thames

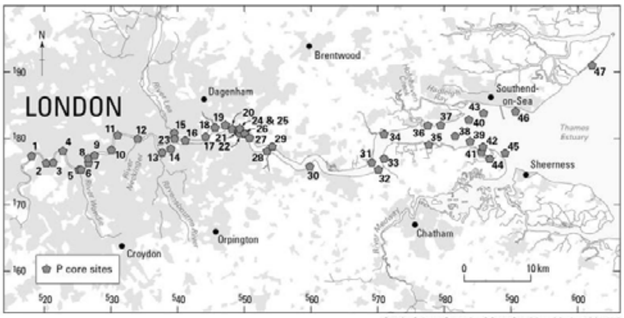

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Figure 2: Map of sampling sites for grab samples (0-3cm) taken from the tidal River Thames

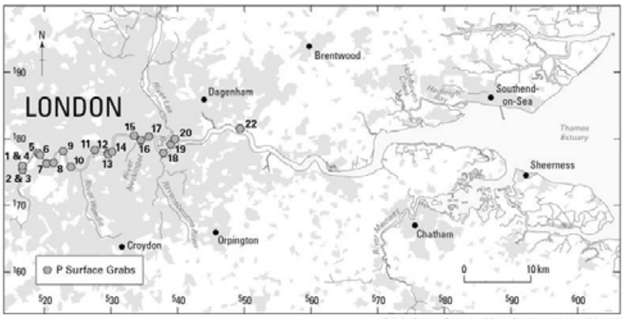

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Figure 3: Characteristics of sediment geochemistry. Graphs (a) and (b) show the relationship between the mean concentration of total Al and Si in the cores with distance from Teddington Lock respectively. In graph C the relationship between total Al and Rb in the 10 cm sediment core sections from all samples are shown (n=260) demonstrating that the sediment is largely derived from one well mixed source throughout the estuary.

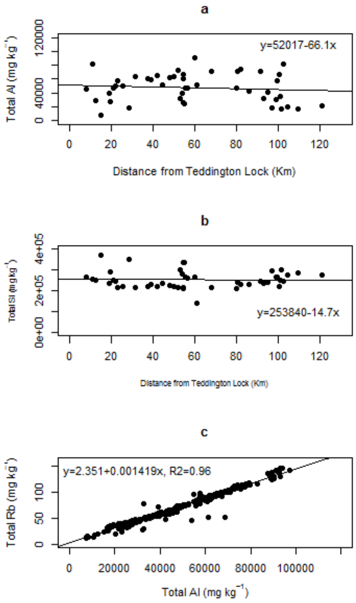


Figure 4: Graph showing (a) sediment depth of cores (cm), (b) a typical salinity (ppt) profile for the tidal Thames taken from Pope & Langston (2011) and (c) mean P_{Total} concentrations (mg kg^{-1}) for the cores. All are plotted against the distance of the sample from Teddington Lock.

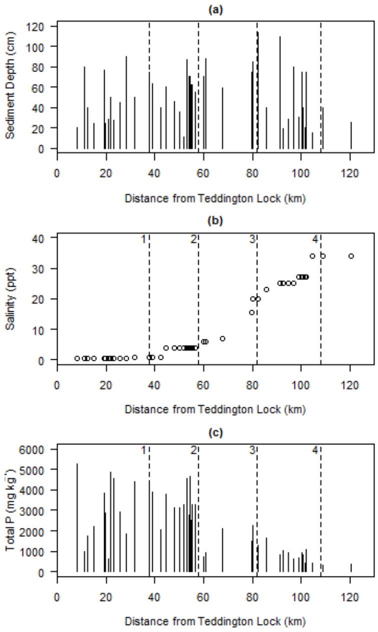


Figure 5: Box and Whisker plots showing the variation in concentration of P_{Total} in 10 cm core sections of cores taken from each of the four estuary zones designated by Littlewood and Crossman (2003) and the grab samples (0-3cm) taken in Zones 1 and 2. The zones are shown in order of distance from Teddington Lock.

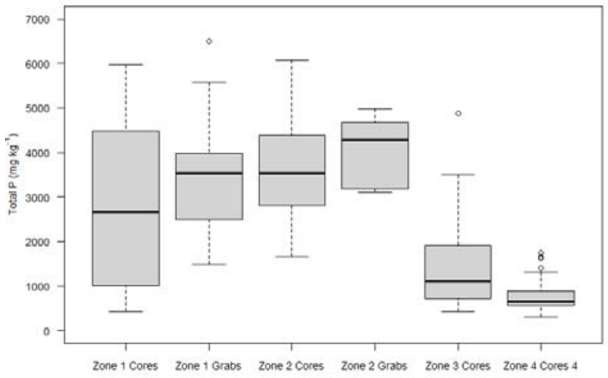


Figure 6: Correlations of P_{Total} with other elements associated with the sequestration of Phosphorus

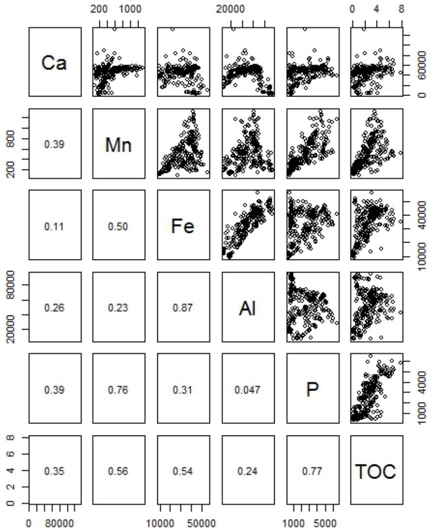


Figure 7: BSEM images taken at 20 kV. Figure 7A (Core 35, depth 10-20 cm) illustrates the ubiquity of FeS_2 (pyrite) in the sediment as the widespread, locally clustered, bright areas. Figure 7B (Core 29, 40-50 cm) shows clustered, framboidal, pyrite.

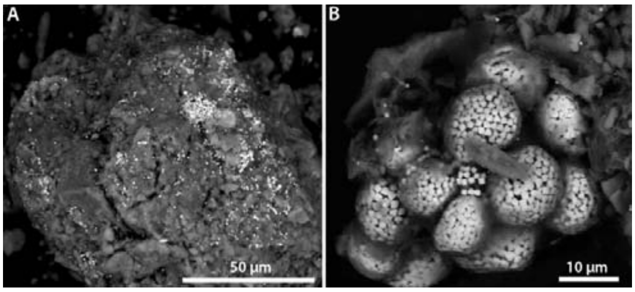


Figure 8: Observed v Predicted regression model for Log P_{Total} for muddy flat sediments in the tidal river Thames. Results of the regression model can be seen in Table 1.

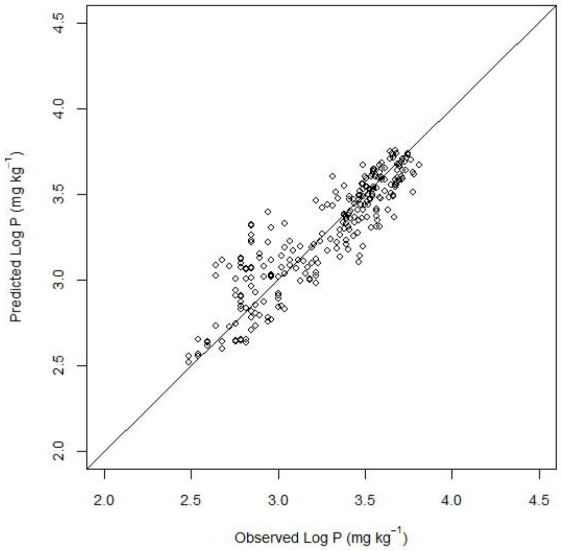


Fig 9: The relationships between oxalate extractable and total concentrations for (a) Fe, (b) Al and (c) and Mn which act as binding surfaces for P in river sediments. In Figures (a) and (b) closed symbols represent samples from Zone 1 and 2 whilst open symbols represent samples from Zones 3 and 4.

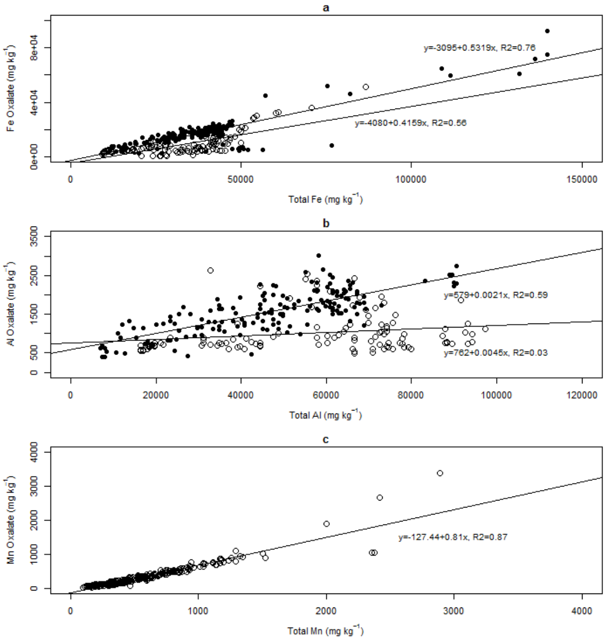


Fig 10: The relationship between P_{Total} and $P_{Oxalate}$ in foreshore sediments of the River Thames.

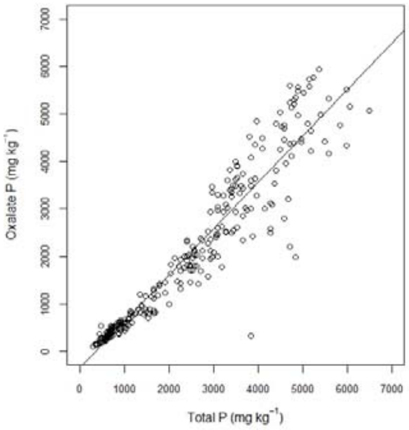


Fig 11: Boxplot showings the range of values of P_{Total}:$P_{Oxalate}$ from Zones 1 and 2 and those from Zones 3 & 4 demonstrating the change in this relationship with increasing salinity.

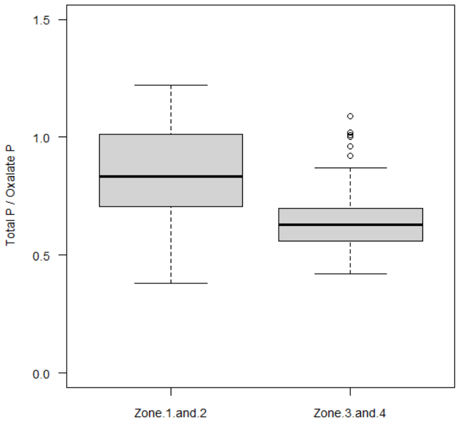


Figure 12: Correlation relationships shown between oxalate extractable P, Al, Mn and Fe in Thames sediments

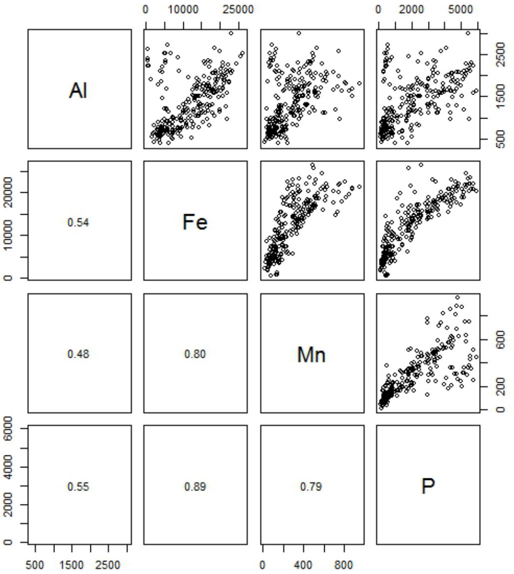


Figure 13: Box and whisker plots to show the range of the Degree of Phosphorus saturation (DSP) in Thames sediments from the four sediment zones and grab samples taken from Zones 1 and 2.

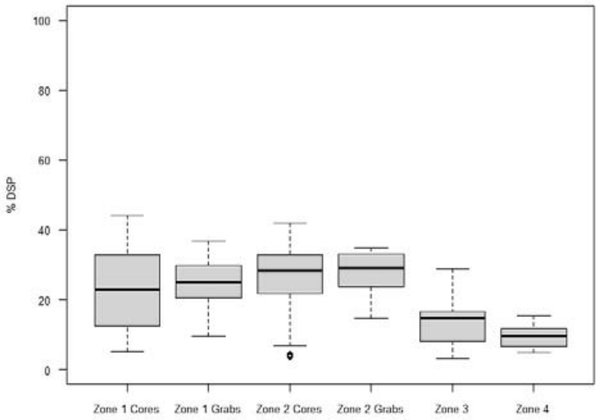


Figure 14: Observed v predicted for model describing the relationships of Log $P_{Oxalate}$ to binding phases in Thames foreshore sediments. Results of the regression model can be seen in Table 2.

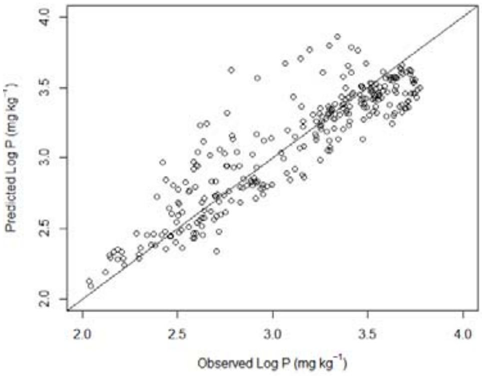


Figure 15: The relationship between concentrations of NaOH extractable $P_{Inorganic}$ and $P_{Organic}$ in three depth segments (0-10 cm, 30-40 cm and 50-60 cm) in cores with distance from Teddington Lock. Cores in Zone 1 are those numbered 1 - 12, in Zone 2 core number 13 - 27, in Zone 3 cores are numbered 28 - 33 and Zone 4 cores are numbered 34 – 47.

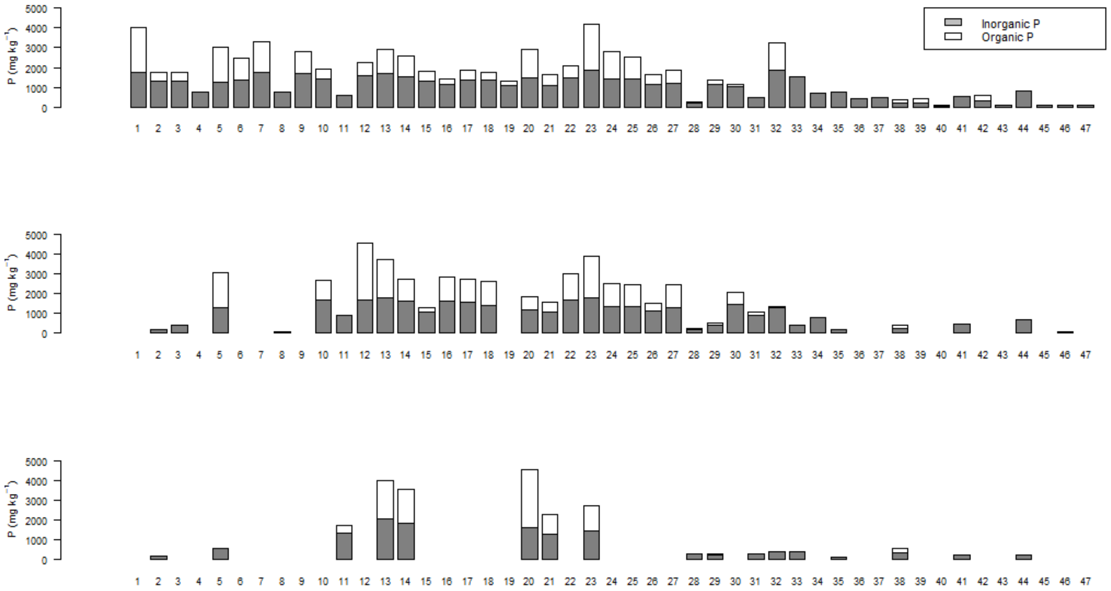


Figure 16: Observed v predicted for model describing the relationships of Log $P_{Inorganic}$ extracted using NaOH to binding phases in Thames foreshore sediments. Results of the regression model can be seen in Table 3. Solid line is the 1:1 line.

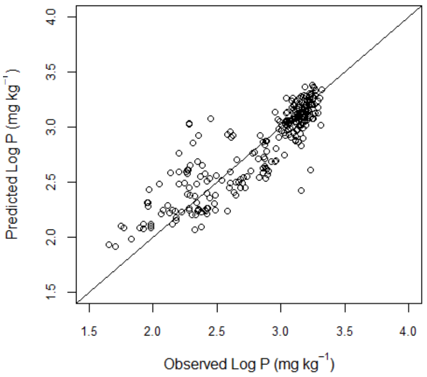
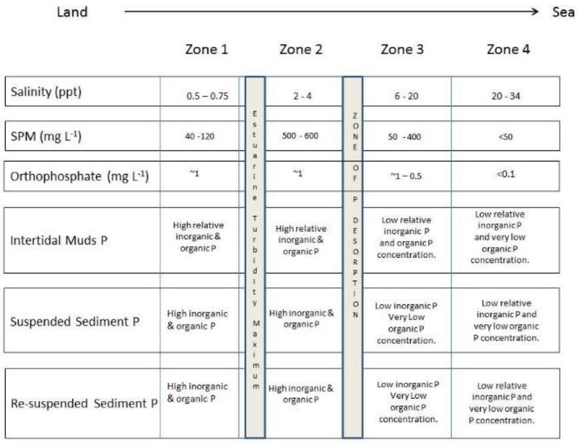


Figure 17: Conceptual model of sediment P behaviour in the Thames estuary based on data from this study on inter-tidal mud deposits. The sediment zones of Littlewood and Crossman (2003) are used with salinity values from Pope and Langston (2011).



Land → Sea

	Zone 1		Zone 2		Zone 3	Zone 4
Salinity (ppt)	0.5 – 0.75	Estuarine Turbidity Maximum	2 - 4	ZONE OF P DESORPTION	6 - 20	20 - 34
SPM (mg L^{-1})	40 -120		500 - 600		50 - 400	<50
Orthophosphate (mg L^{-1})	~1		~1		~1 – 0.5	<0.1
Intertidal Muds P	High relative inorganic & organic P		High relative inorganic & organic P		Low relative inorganic P and organic P concentration.	Low relative inorganic P and very low organic P concentration.
Suspended Sediment P	High inorganic & organic P		High inorganic & organic P		Low inorganic P Very Low organic P concentration.	Low relative inorganic P and very low organic P concentration.
Re-suspended Sediment P	High inorganic & organic P		High inorganic & organic P		Low inorganic P Very Low organic P concentration.	Low relative inorganic P and very low organic P concentration.