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# Phosphorus sorption in soils and sediments: implications for phosphate supply to a subtropical river in southeast Queensland, Australia

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**Abstract** Phosphorus (P) is often a key limiting nutrient in freshwater systems, and excessive P can result in algal blooms, with flow-on effects to aquatic food webs. P sorption is an important process in aquatic and terrestrial ecosystems whereby phosphate ($PO_4^{3-}$) is exchanged between liquid and solid phases. This study shows that differences in the concentration of $PO_4^{3-}$ in a subtropical river system during high and low flow can be attributed to differences in P sorption characterises of its catchment soils and sediments. The sediments have lower Equilibrium Phosphate Concentrations ($EPC_0$) and higher binding energy ($K_d$); the surface soils have higher $EPC_0$ and higher easily desorbed P ($NH_4Cl$–P). A comparison of filterable reactive phosphorus (frP) in water samples collected at high and low flows, with soil and sediment $EPC_0$, suggested that during event flows, the high $EPC_0$ and $NH_4Cl$–P of surface soils is producing a net movement of $PO_4^{3-}$ from the soil/sediment system into runoff and stream flow. At baseflow, there is more likely a net movement of $PO_4^{3-}$ into the riverbed sediments. This has important implications for management actions aimed at reducing P loads to river systems and downstream water storages, namely the need to increase the infiltration of rainfall to decrease the amount of $PO_4^{3-}$ being flushed from the surface soil.

**Keywords** Equilibrium phosphate concentration · Phosphorus · Rivers · Sediment · Soil

## Introduction

P sorption is an important process in aquatic and terrestrial ecosystems whereby phosphate ($PO_4^{3-}$) is exchanged between liquid and solid phases. The exchange of P between soils/sediments and the water column via sorption processes has been described in terms of the Equilibrium Phosphorus Concentration ($EPC_0$). At equilibrium the concentration of $PO_4^{3-}$ in the water column is largely determined by adsorption and desorption exchanges with the sediments. If the concentration of $PO_4^{3-}$ in solution increases above equilibrium concentration, then more $PO_4^{3-}$ will adsorb onto solid surfaces to re-establish the equilibrium condition. Conversely, if the concentration in solution were to fall, then $PO_4^{3-}$ would be desorbed

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from the solid sediment phase (Froelich 1988; House and Denison 2000, 2002; Jarvie et al. 2005).

Within river systems, sorption reactions can buffer water column $PO_4^{3-}$, which may be an important factor controlling the supply to in-stream primary producers, and also downstream in lakes, reservoirs and estuaries (House et al. 1995; James and Barko 2004; Mainstone and Parr 2002). Using estimates of the $EPC_0$ of sediments and the $PO_4^{3-}$ concentration in the water column, researchers have reported that bed sediments can function as both a net sink (House and Warwick 1998a, 1999) and a net source for $PO_4^{3-}$ (Jarvie et al. 2005). This will depend on not just the sorption properties of the sediments but also on the processes which supply $PO_4^{3-}$ to the river system. Importantly, sediments with low $EPC_0$ may still function as a source if ambient water column $PO_4^{3-}$ is low, while sediments with higher $EPC_0$ may act as a sink where water column $PO_4^{3-}$ is high. Therefore, a comparison of ambient water column $PO_4^{3-}$ with the $EPC_0$ of riverbed sediments can shed substantial light on the in-stream dynamics of $PO_4^{3-}$. However, to better understand $PO_4^{3-}$ dynamics at the catchment scale it is important to also consider sorption exchanges which occur between soils and overland and subsurface flows during rain events.

In soils, sorption reactions are important when soils come into contact with water. Many transport models developed to simulate P loss from cultivated fields include the desorption of P from the soil to the runoff water as the source of $PO_4^{3-}$ (Yli-Halla et al. 1995). The $EPC_0$ of soils can be used as an indicator of the potential for desorption of $PO_4^{3-}$ from soils (Fang et al. 2002; McDowell and Sharpley 2003). Aquatic ecosystems downstream are linked to the catchments soil/sediment system via hydrological flow pathways with the movement of $PO_4^{3-}$ along these paths determined by flow and the affinity of the soil/sediment system for P (Nash and Halliwell 2000). Therefore, it is clear that at the catchment scale, sorption reactions across the entire soil/sediment system are important to the flux of $PO_4^{3-}$ through the system.

A range of physiochemical properties of soils and sediments have been identified as being important determinants of P sorption. Several key properties including amorphous and poorly crystalline forms of Fe and Al (Bolland et al. 1996; McDowell and Sharpley 2001; Pant and Reddy 2001), redox conditions (Olila and Reddy 1997; Pant and Reddy 2001; Rhue and Harris 1999), organic matter content (Borggaard et al. 2005; Yoo et al. 2006), particle size distribution of sediments/soils (House and Warwick 1999; Lottig and Stanley 2007; Meyer 1979) and pH (Bolland et al. 1996; Eckert et al. 1997; Yoo et al. 2006) have been found to be associated with P sorption. Importantly, several of these factors are likely to differ substantially between terrestrial and aquatic environments. This in turn may result in differences in P sorption between river sediments and the soils from which they were derived. The majority of data on P sorption comes from studies of either soil (terrestrial) or sediment (aquatic) and there is a lack of data comparing P sorption in soils and sediments within the same system. This is an important knowledge gap because to properly understand P fluxes at the catchment scale it is important to firstly quantify P sorption across the entire soil/sediment system, and secondly to identify the major physiochemical properties which drive P sorption variability at the catchment scale.

The aims of this study were to determine if there are differences in P sorption between sediments and soils of a subtropical river catchment. The study also aimed to identify the major variables governing P sorption properties across the entire soil/sediment system. Finally, the study aimed to identify the importance of P sorption across the entire catchment in terms of controlling water column $PO_4^{3-}$ under high and low flow conditions.

## Methods

### Study area

The study was conducted in the upper Brisbane River (UBR) catchment in southeast Queensland, Australia, approximately 80 km northwest of the city of Brisbane. The area has particular significance because the UBR flows into southeast Queensland's largest potable water storage at Lake Wivenhoe. Like much of southeast Queensland, land use is dominated by cattle grazing (69%) and there is considerable hillslope and gully erosion. There are no substantial industrial land uses in the catchment so P inputs are derived predominately from diffuse sources. There is little intensive agriculture and associated fertiliser application in the catchment and intensive animal uses such as dairy farming constitute only 4% of total land use. Despite this $PO_4^{3-}$ often constitutes a substantial proportion of total P (TP) during event flows, particularly at sites in the UBR (Kerr 2009).

### Study sites and sampling

Samples were collected at sites along the UBR and Emu Creek over 3 days in February 2007. Sites ranged from the upper catchment at UBR17 to the lower catchment immediately upstream of Lake Wivenhoe (UBRO). The location of study sites corresponded to three major rock types identified by Douglas et al. (2007) as being the principal sources of sediment and P to Lake Wivenhoe. Five sites were located in the Neara Volcanics, two sites in the Esk Formation and one site from the Maronghi Creek Beds (Fig. 1). At each site, samples were collected of bed sediment and potential source material from the adjacent surface soils and also from streambank soils. All samples were collected from the top 2 cm of sediment or soil using PVC cores or a steel trowel. In this study surface soils are defined as the top 2 cm of soil in areas upland of each site. Streambank soils are defined as the top or outer 2 cm of streambank soil between the top of the streambank and the water level. For each soil type (sediment, streambank and surface), three cores were taken from each sampling point and homogenised to form a composite sample with a total of five composite samples for each soil type at each site. Sediment samples were stored in zip lock bags placed inside larger bags filled with sediments to avoid oxidation of bed sediments during collection and storage (Baldwin 1996). All samples were stored on ice prior to being frozen in the laboratory. Water samples were also collected from each study site and filtered through 0.45 μm membrane filters (Millipore, U.S.A) and determined for filterable reactive phosphorus (frP) based on the method of Murphy and Riley (1962). fRP is an operationally defined term analogous to soluble reactive phosphorus or dissolved reactive phosphorus and is thought to be a close representation of $PO_4^{3-}$.

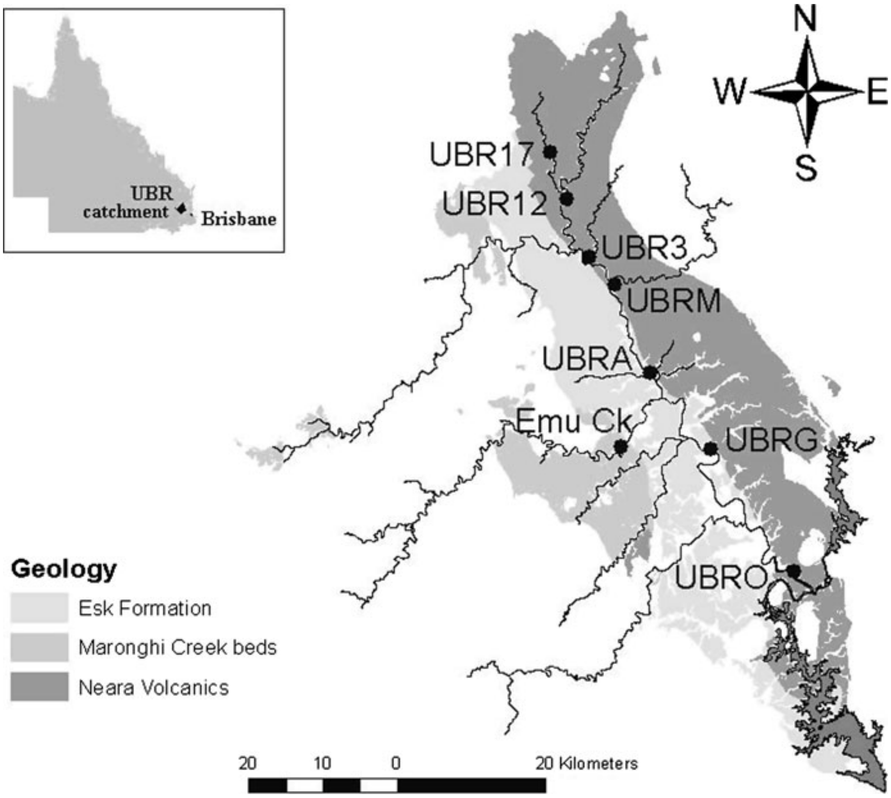

**Fig. 1** Location of sampling sites within the upper Brisbane River catchment

## Sediment characteristics

Soil and sediment pH was determined using a pH electrode in a 1:2 slurry of soil:deionized water (Darke and Walbridge 2000). Organic matter was determined as loss on ignition (LOI) by recording the ratio of the weight loss at 560°C and the original dry weight of sample (Qui and McComb 2002). Bulk density was determined by weighing a known volume of sample after drying (Buurman et al. 1996) while percent moisture content was determined gravimetrically by drying 15–35 g aliquots of each bulk sample to a constant mass at 60°C (Darke and Walbridge 2000). Particle size analysis was determined by sieving a dried sample through a set of sieves of decreasing aperture ranging from 2 mm to 63 µm (Gordon et al. 1992). Amorphous and poorly crystalline forms of Fe and Al were determined through extraction in a 0.2 M acid oxalate solution for 4 h in the dark on an end over end shaker (Buurman et al. 1996). Fe and Al were then determined in the extracts using Flame Atomic Adsorption Spectrophotometry (GBC Avanta Sigma, Melbourne).

## Sequential extraction

Samples for sequential extraction were sieved through 1 mm mesh and then ground using a Retsch MM200 mixer mill (Haan, Germany). Sequential phosphorus extraction was carried out using the SMT protocol (Pardo et al. 2004; Ruban et al. 1999, 2001). The SMT protocol is an operationally defined scheme based on the Williams method which separates sediment P into five fractions using three leaching procedures applied to separate samples. The procedure involved extracting (16 h) the P bound to Fe, Al and Mn oxyhydrates with 1 M NaOH followed by treatment of an aliquot of the NaOH extract with 3.5 M HCl to determine Non Apatite Inorganic Phosphorus (NAIP). The residue of this extraction was then extracted (16 h) with 1 M HCl to remove the Ca-bound P associated with carbonates to determine Apatite Inorganic Phosphorus (AIP). On a separate sample, an extraction (16 h) using 1 M HCl was performed to remove Inorganic Phosphorus (IP) with the residue dried, calcinated at 450°C for 3 h and treated with 1 M HCl to remove the phosphorus associated with Organic Phosphorus (OP). Total Phosphorus (TP) was obtained on a separate sample by calcination at 450°C for 3 h followed by extraction (16 h) with 3.5 M HCl (Pardo et al. 2004). In addition to the SMT protocol, samples were also measured for exchangeable P ($NH_4Cl$–P). 0.5 g dry weight equivalent of sediment was weighed into 50 ml centrifuge tubes, 25 ml 1.0 M $NH_4Cl$ was added and the pH adjusted to 7. The mixture was shaken for 2 h and the supernatant separated by centrifugation at 4000 × *g* and filtered through 0.45 µm membrane filters (Millipore, U.S.A) (Psenner et al. 1988). All soil and sediment extracts were determined for frP based on the method of Murphy and Riley (1962).

Concentration data for different P fractions were extrapolated to estimate pool sizes in each of the soil/sediment groups. Estimates were based on conversion of data from mass to area using bulk density data for the top 2 cm of soil or sediment and multiplication by the total area of each soil/sediment type. Surface soil pools were categorised into the three rock types identified by Douglas et al. (2007) as being the principle sources of sediment and P to Lake Wivenhoe. The area of each rock type was calculated using GIS software from maps provided by the Queensland Department of Natural Resources and Water. For sediments, the total streambed area was calculated for the UBR and tributaries based on a total length of 469 km and a stream width of 19 m (Kerr 2009). The streambank soil area was estimated based on a total length of 469 km and an estimated 2 $m^2$ of exposed streambank per metre of stream length.

## Phosphorus sorption

The P sorption characteristics of sediment and soils were determined using batch equilibrium experiments based on the method of Nair et al. (1984). 0.5 to 1 g (dry weight equivalent) of sieved (<1 mm) soil and sediment samples were placed into 50 ml centrifuge tubes and treated with two drops of chloroform to inhibit microbial uptake, and 25 ml of standard phosphorus solutions ranging in concentration from 0 to 100 mg $l^{-1}$. Standard phosphorus solutions were prepared using analytical grade anhydrous $KH_2PO_4$ in a 0.01 M CaCl matrix. Samples were equilibrated at 25 ± 2°C in an end over end shaker for 24 h before being centrifuged at 4000 × *g* for 15 min. The supernatant was then filtered through 0.45 µm membrane filters (Millipore, U.S.A) and determined for frP based on the method of Murphy and Riley (1962).

The amount of P retained by the sediment and soil at equilibrium (S′, mg kg$^{-1}$ dry wt.) was calculated as the difference between the concentration of P in solution at 24 h and at 0 h. The P sorption maximum ($S_{max}$, mg kg$^{-1}$) and bonding energy constant (k, l mg$^{-1}$) were estimated using the Langmuir equation (Pant and Reddy 2001). A plot of S′ and the equilibrium frP concentration (C, mg l$^{-1}$) at low equilibrium concentration was used to calculate the native sorbed P ($S_0$, mg kg$^{-1}$ dry wt.), the linear adsorption coefficient ($K_d$, l kg$^{-1}$) and the equilibrium phosphate concentration ($EPC_0$, mg l$^{-1}$) (House and Denison 2000; Pant and Reddy 2001).

### Statistical analysis

Statistical analyses were performed using the Statistical Package for the Social Sciences (SPSS) version 14.0.1. Variations in mean values were calculated and reported as standard deviations. All samples were assessed for normality (Shapiro–Wilk test) and homogeneity of variance (Levenes test). When the assumption of homogeneity of variance was violated, data were transformed using a logarithmic transformation. Statistical differences between soil types were calculated using one way or two way ANOVA. Non-parametric Mann–Whitney test were conducted where homogeneity of variance could not be achieved through logarithmic transformation. The degree to which the variation between two or more variables was shared was investigated using correlation and multiple regression analysis.

## Results

The physiochemical properties of soils and sediments varied substantially within the catchment (Table 1). A comparison of soil pools found that there were significant differences between soil and sediments for pH, bulk density and $Fe_{ox}$. Sediments had significantly lower bulk density relative to soils ($P < 0.05$) while pH and $Fe_{ox}$ were significantly lower ($P < 0.05$) in surface soils. There were no clear spatial patterns in $Fe_{ox}$ in the catchment apart from at Emu Ck where $Fe_{ox}$ was lowest for soils and sediment. $Al_{ox}$ was similar between the different soil pools and was generally higher in the upper catchment (UBR17–UBR12). The proportion of fine material (% fines) was also highest in the upper reaches for both soils and sediments. In terms of differences between soil pools, streambank soils had lower % fines relative to surface soils and sediments. LOI and TP showed a similar pattern to % fines with the highest LOI and TP in the upper reaches of the catchment (UBR17–UBR12) (Table 1).

### Phosphorus fractionation of sediments and soils

Sediment and soil P within the catchment was dominated by the AIP fraction making up between 40 and 70% of TP. There was a general trend of higher AIP in the upper reaches of the catchment and a gradual decrease in the lower catchment for soils and sediments. Although there were significant differences between soil pools at most sites (Fig. 2), there was no consistent pattern in terms of differences in AIP between soils and sediments. NAIP and OP also made up a substantial proportion of TP within the catchment. As a proportion of TP, NAIP ranged from 13 to 33% while OP comprised between 19 and 34%. NAIP and OP exhibited a similar spatial distribution across the catchment and there was a strong positive correlation between the two fractions (Table 2). NAIP and OP were both positively correlated with % fines and LOI. However, the strongest correlation for both of these fractions was with $Al_{ox}$ (Table 2). The $NH_4Cl$–P fraction did not exhibit the same spatial patterns as the NAIP, OP and AIP fractions and was not correlated with any of the fractions measured using the SMT protocol (Table 2). Across all three soil pools the concentration of $NH_4Cl$–P was negatively correlated with $Fe_{ox}$ and pH. Unlike the other fractions, mean $NH_4Cl$–P was significantly lower in sediments relative to streambank and surface soils at most sites. Mean $NH_4Cl$–P was highest in the surface soils of UBR12, UBRA and UBRO which was different than the NAIP and OP fractions.

### Phosphorus sorption in sediment and soil

Overall the sediments exhibited a much greater affinity for added P relative to the surface soils and to a lesser extent the streambank soils (Table 3). Sediment and streambank soil $S_{max}$ was significantly

**Table 1** Physiochemical properties and TP of sediments, streambank soils and surface soils

| | pH | % LOI | % Fines | $Fe_{ox}$ ($mg\ g^{-1}$) | $Al_{ox}$ ($mg\ g^{-1}$) | Bulk density ($mg\ cm^{-3}$) | TP ($mg\ kg^{-1}$) |
|---|---|---|---|---|---|---|---|
| Bed sediment | | | | | | | |
| UBR17 | 7.29 | 14.2 | 43.7 | 4.07 | 1.11 | 0.62 | 732 |
| UBR12 | 7.12 | 12.6 | 33.4 | 2.76 | 1.12 | 0.75 | 707 |
| UBR3 | 7.22 | 2.4 | 11.4 | 2.38 | 0.9 | 1.41 | 478 |
| UBRM | 7.31 | 5.9 | 16.6 | 2.71 | 0.86 | 0.9 | 446 |
| UBRA | 7.23 | 9.5 | 26.1 | 4.42 | 1.06 | 0.59 | 539 |
| UBRG | 6.96 | 8.8 | 10.1 | 2.19 | 0.85 | 0.89 | 497 |
| UBRO | 6.5 | 1.2 | 8.1 | 2.44 | 0.68 | 1.12 | 528 |
| Emu Ck | 7.45 | 1.3 | 2.1 | 0.7 | 0.24 | 1.32 | 174 |
| Streambank soil | | | | | | | |
| UBR17 | 7.08 | 8.19 | 7.8 | 2.31 | 0.96 | 1.55 | 798 |
| UBR12 | 7.35 | 12.34 | 10.2 | 1.87 | 1.31 | 1.76 | 728 |
| UBR3 | 7.2 | 4.31 | 8.1 | 3.09 | 0.6 | 1.62 | 572 |
| UBRA | 7.47 | 6.49 | 9.2 | 2.58 | 0.76 | 1.51 | 545 |
| UBRG | 7.33 | 3.81 | 6.5 | 1.57 | 0.73 | 1.61 | 366 |
| UBRO | 6.5 | 3.93 | 8.9 | 3.49 | 0.85 | 1.75 | 434 |
| Emu Ck | 7.4 | 5.02 | 7.7 | 1.47 | 0.68 | 1.63 | 350 |
| Surface soil | | | | | | | |
| UBR17 | 6.77 | 9.67 | 20.6 | 1.13 | 1.14 | 1.41 | 1019 |
| UBR12 | 6.44 | 11.41 | 23.5 | 1.04 | 1.02 | 1.33 | 968 |
| UBR3 | 6.55 | 8.88 | 15.2 | 1.01 | 0.86 | 1.45 | 600 |
| UBRM | 6.36 | 4.47 | 11.2 | 1.15 | 0.85 | 1.52 | 537 |
| UBRA | 6.45 | 3.63 | 10 | 1.11 | 0.75 | 1.62 | 543 |
| UBRG | 6.22 | 3.65 | 9.1 | 0.88 | 0.58 | 1.59 | 397 |
| UBRO | 5.92 | 5.32 | 17.7 | 0.82 | 0.67 | 1.21 | 488 |
| Emu Ck | 6.92 | 3.57 | 21.3 | 0.75 | 0.49 | 1.39 | 377 |

higher than surface soils ($P < 0.05$) but there was no significant difference in $S_{max}$ between sediments and streambank soils ($P > 0.05$). There was a strong positive correlation between $S_{max}$ and $Fe_{ox}$ (Table 2). The linear adsorption coefficient ($K_d$) was significantly higher in streambed sediments than in surface or streambank soils ($P < 0.05$) and streambank soil $K_d$ was significantly higher than in surface soil ($P < 0.05$). There was a strong negative correlation between $K_d$ and $EPC_0$ and $NH_4Cl$–P, and a positive correlation between $K_d$ and $Fe_{ox}$ (Table 2). The $EPC_0$ values within the catchment also varied significantly ($P < 0.05$) between sediments and soils (Table 3). With the exception of Emu Ck, the $EPC_0$ values were lower in sediments than in either surface or streambank soils at all sites. Apart from Emu Ck, the $EPC_0$ was higher in surface soils than in streambank soils at all sites. For $EPC_0$ there was a negative correlation with $Fe_{ox}$ and pH and a positive correlation with $NH_4Cl$–P (Table 2). Multiple stepwise regression analysis demonstrated a significant relationship ($P < 0.01$) between log $EPC_0$ and $Fe_{ox}$ and $NH_4Cl$–P. Together log $Fe_{ox}$ and log $NH_4Cl$–P explained approximately 76% of the variation in log $EPC_0$.

### Comparison of the $EPC_0$ of soils and sediments with water column frP under event flow and baseflow conditions

The $EPC_0$ of soils and sediments in different regions of the catchment have been compared with historical event flow (2003–2006) and baseflow (2005–2007)

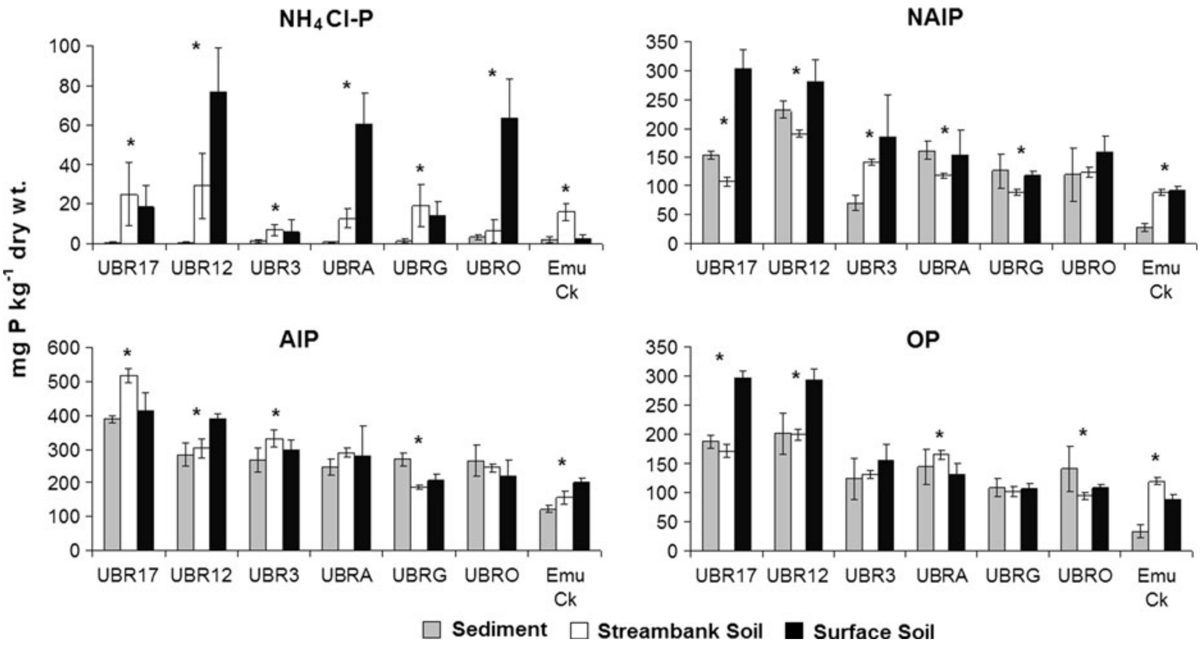

**Fig. 2** P speciation for each site and soil type (* indicates a significant difference between soil types at each site)

**Table 2** Correlation coefficient (*r*) matrix for measured variables

| | % Fines | $Fe_{ox}$ | $Al_{ox}$ | pH | $NH_4Cl$–P | NAIP | AIP | OP | $EPC_0$ | $K_d$ | $S_{max}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| LOI | 0.694** | 0.285 | 0.761** | 0.112 | 0.035 | 0.714** | 0.585** | 0.707** | −0.185 | 0.163 | 0.378 |
| % Fines | | 0.229 | 0.680** | −0.148 | −0.207 | 0.718** | 0.505* | 0.691** | −0.358 | 0.383 | 0.345 |
| $Fe_{ox}$ | | | 0.521* | 0.435* | −0.453* | 0.141 | 0.379 | 0.285 | −0.645** | 0.731** | 0.807** |
| $Al_{ox}$ | | | | −0.010 | 0.039 | 0.774** | 0.708** | 0.865** | −0.204 | 0.294 | 0.515* |
| pH | | | | | −0.421* | −0.407 | −0.089 | −0.121 | −0.566** | 0.514* | 0.252 |
| $NH_4Cl$–P | | | | | | 0.254 | 0.119 | 0.228 | 0.830** | −0.858** | −0.379 |
| NAIP | | | | | | | 0.658** | 0.878** | 0.116 | −0.079 | 0.229 |
| AIP | | | | | | | | 0.794** | 0.063 | 0.040 | 0.288 |
| OP | | | | | | | | | 0.013 | 0.037 | 0.352 |
| $EPC_0$ | | | | | | | | | | −0.941** | −0.576** |
| $K_d$ | | | | | | | | | | | 0.657** |

* Sig 0.05; ** sig 0.01

frP concentrations at corresponding sites (Fig. 3). In the upper (UBR17–UBR3) and lower reaches (UBRA–UBRO) of the UBR, the median frP at baseflow was similar to the average $EPC_0$ of bed sediments. In contrast, the median event flow frP was more similar to average streambank $EPC_0$, particularly in the upper reaches. In both regions the surface soil $EPC_0$ was substantially higher than event flow frP. For Emu Ck the patterns observed between measured $EPC_0$ in soils and sediments and historical frP were very different to the UBR. At Emu Ck, median event flow frP concentration was more similar to surface soil $EPC_0$ than to streambank soil. Furthermore, unlike the UBR, the frP at baseflow was not similar to the $EPC_0$ of either sediments or streambank soils. On a whole of catchment basis, the median event flow frP concentration was similar to streambank soil $EPC_0$ and the baseflow frP was similar to the average sediment $EPC_0$ (Fig. 3).

**Table 3** Sorption properties of streambed sediment, streambank soil and surface soil in the UBR catchment

| Site | $K_d$ (l kg$^{-1}$) | $S_0$ (mg kg$^{-1}$) | $EPC_0$ (mg l$^{-1}$) | $S_{max}$ (mg kg$^{-1}$) | k (l mg$^{-1}$) | Kf |
|---|---|---|---|---|---|---|
| Strementbed sediment | | | | | | |
| UBR17 | 7131.1 | 4.3 | 0.001 | 2417.6 | 1.509 | 1034.2 |
| UBR12 | 6247.4 | 14.3 | 0.002 | 1685.9 | 1.209 | 681.9 |
| UBR3 | 2300.4 | 38.0 | 0.017 | 1155.3 | 0.152 | 222.8 |
| UBRM | 1076.5 | 12.1 | 0.011 | 1220.6 | 0.349 | 321 |
| Emu Ck | 119.7 | 8.0 | 0.067 | 159.9 | 0.995 | 69.9 |
| UBRA | 6351.1 | 0.9 | 0.001 | 2534.4 | 0.816 | 885.7 |
| UBRG | 384.6 | 7.5 | 0.020 | 648.2 | 0.129 | 82.3 |
| UBRO | 497.3 | 18.0 | 0.036 | 602.9 | 0.179 | 103.8 |
| Streambank soil | | | | | | |
| UBR17 | 129.1 | 19.5 | 0.151 | 1029.9 | 0.045 | 42.1 |
| UBR12 | 156.6 | 22.8 | 0.145 | 765.2 | 0.063 | 59.4 |
| UBR3 | 223.1 | 17.3 | 0.077 | 1473.7 | 0.027 | 49.6 |
| Emu Ck | 141.4 | 11.7 | 0.083 | 1148.6 | 0.025 | 50.5 |
| UBRA | 258.1 | 9.3 | 0.036 | 1058.8 | 0.031 | 63.7 |
| UBRG | 244.0 | 11.4 | 0.047 | 327.4 | 0.209 | 57.3 |
| UBRO | 475.8 | 26.9 | 0.056 | 2099.6 | 0.144 | 87.8 |
| Surface soil | | | | | | |
| UBR17 | 64.7 | 10.8 | 0.166 | 511.6 | 0.065 | 37 |
| UBR12 | 27.7 | 32.8 | 1.182 | 524.8 | 0.025 | 12.4 |
| UBR3 | 66.0 | 14.2 | 0.215 | 329.3 | 0.091 | 33.1 |
| UBRM | 177.8 | 15.9 | 0.090 | 968.4 | 0.05 | 58.6 |
| Emu Ck | 295.9 | 8.3 | 0.028 | 148.2 | 0.558 | 49.3 |
| UBRA | 19.5 | 24.3 | 1.244 | 92.8 | 0.123 | 18.9 |
| UBRG | 55.8 | 8.2 | 0.147 | 839.3 | 0.036 | 35.3 |
| UBRO | 37.1 | 37.0 | 0.997 | 550.1 | 0.068 | 40.6 |

### Comparison of $NH_4Cl$–P pools, P sorption capacity and annual frP loads in the UBR catchment

There were large stores of NAIP, AIP and OP in the surface soils. These pools were distributed predominately between the Neara Volcanics and Esk Formations and were orders of magnitude greater than in the sediments or streambank soils (Fig. 4). Total sediment P storage was approximately three times higher than the maximum annual TP export at UBRG while streambank soil P was considerably lower. Like the NAIP, AIP and OP fractions, the estimated mass of $NH_4Cl$–P in the surface soils was orders of magnitude greater than the $NH_4Cl$–P stores in the sediments and streambank soils (Table 4). The annual frP loads were approximately 2–20 times higher than the sediment and streambank soil $NH_4Cl$–P stores. The potential sorption capacity of the sediments was substantially higher than annual frP loads but less than 10% of the surface soil $NH_4Cl$–P stores (Table 4).

## Discussion

This study provides important new findings comparing P sorption across the soil/sediment system of a catchment, as there are few studies that have taken a whole of catchment approach. This study has shown that differences in the concentration of frP in the river system during high and low flow can be attributed to differences in P sorption and speciation between soils and sediments. During event flows, the high $EPC_0$ and $NH_4Cl$–P of surface soils would be expected to produce a net movement of $PO_4^{3-}$ from the soil/sediment system to runoff and stream flow. At

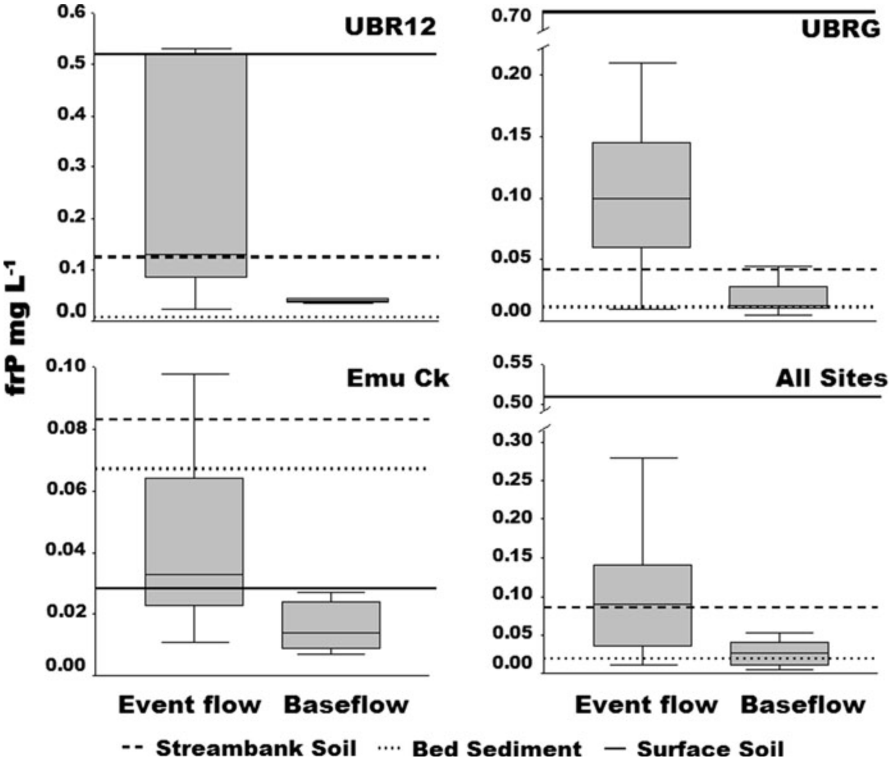

**Fig. 3** Comparison of $EPC_0$ in soils and sediments with event and baseflow frP (*box* and *whisker plots*) at UBR12, UBRG and Emu Ck. *Source*: Seqwater event monitoring data 2004–2006 (event flow) and Kerr (2009) (2005–2006) (baseflow)

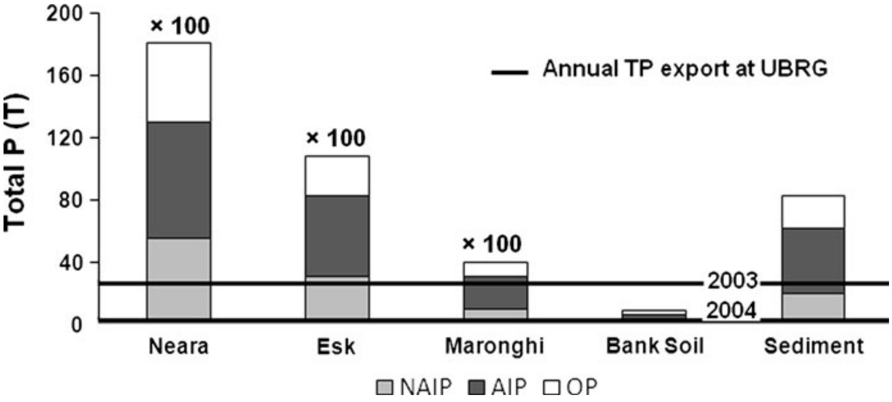

**Fig. 4** Comparison of P pools in soils and sediments and minimum and maximum annual TP export at UBRG from 2003 to 2006

**Table 4** Estimated $NH_4Cl$–P pools (T) in surface, streambank soils and sediments and comparison with potential sediment sorption capacity and the minimum and maximum annual frP loads at UBRG from 2003 to 2006

| Surface soil | | | Streambank soil | Bed sediment | Sediment sorption capacity | Annual frP load[a] |
|---|---|---|---|---|---|---|
| Neara | Esk | Maronghi | | | | |
| 966 (713) | 617 (557) | 28 (15) | 0.5 (0.2) | 0.4 (0.4) | 126 (85) | 0.8–11.3 |

[a] From Kerr (2009)

baseflow, there is more likely to be a net movement of $PO_4^{3-}$ into the soil/sediment system across the sediment–water interface. The combination of extremes in P sorption between soils and sediments and the highly variable hydrology which characterises the UBR catchment (Kennard et al. 2009) are likely to be the key drivers of $PO_4^{3-}$ movement through the system. Specifically, these properties of the catchment mean that the system is likely to switch between extremes of retention and loss in terms of $PO_4^{3-}$ dynamics.

A comparison of the $EPC_0$ of bed sediments with baseflow frP indicated that sorption exchanges at the sediment water interface are likely to be an important driver of ambient $PO_4^{3-}$ under low flow conditions. The $EPC_0$ of bed sediments in the UBR were at the lower end of the range of values reported in other studies (House and Warwick 1998b; James and Barko 2004; Lottig and Stanley 2007; McDowell 2003; McDowell and Sharpley 2001; Munn and Meyer 1990; Stutter and Lumsdon 2008). The $EPC_0$ of the catchment soils on the other hand were generally much higher than these values indicating that the high affinity of bed sediments for P was not a reflection of the properties of the wider catchment soil/sediment system. The results from the UBR would suggest a strong role for $Fe_{ox}$ in the high P sorption properties of UBR bed sediments. The particularly high $K_d$ and low $EPC_0$ of sediments in the UBR indicate that there will be a net flux of $PO_4^{3-}$ into the bed sediments via adsorption even at relatively low ambient $PO_4^{3-}$ (i.e. $<0.010$ mg $l^{-1}$ for some sites). Furthermore, $NH_4Cl$–P in the sediments was very low indicating that P was largely bound in metal complexes or held in organic matter and therefore not readily desorbed into the water column (Romero-Gonzalez et al. 2001). During periods of low flow, inputs of $PO_4^{3-}$ to the water column would need to come predominately from the turnover of other P pools such as NAIP and OP. The total NAIP and OP within the bed sediments was large relative to annual TP and frP export from the river system. Therefore the turnover of even small amounts may be significant in terms of catchment scale $PO_4^{3-}$ fluxes. The strong spatial patterns for these two fractions and the association with organic matter and amorphous Al suggests that their importance as a source of $PO_4^{3-}$ will vary across spatial scales and be related to transformation processes involving organic matter and amorphous Al.

The results from the UBR indicate that during storm events there is a large net movement of $PO_4^{3-}$ from the soil/sediment system to the water column. The desorption of $PO_4^{3-}$ from large stores of loosely sorbed P in the surface soils, and to a lesser extent streambank soils, is likely to be a major source of $PO_4^{3-}$ to the river system via overland or stream flow. Due to a combination of increased hydrological connectivity and the poor P buffering capacity of soils, large losses of $PO_4^{3-}$ from the catchment are likely. The results demonstrated that the pools of $NH_4Cl$–P in the surface soils were large enough that even small losses during event flows could easily account for frP exports from the river system. Furthermore, unlike the bed sediments, the $EPC_0$ of surface soils had comparatively poor P buffering capacity. The $EPC_0$ of surface soils at UBR12, UBRA and UBRO was high relative to studies of other soils (Borling et al. 2004; Fang et al. 2002; Gardner et al. 2002; House et al. 1995; Yli-Halla et al. 1995; Zhou and Li 2001). The $EPC_0$ of streambank soils was also considerably higher than values reported for other streambank soils (McDowell 2003; McDowell and Sharpley 2001; Stutter and Lumsdon 2008).

Because the sorption potential of soils is relatively limited, the retention of $PO_4^{3-}$ at high flow will depend largely on the capacity of the existing bed sediments to buffer the higher concentration in the water column. In terms of the $EPC_0$ (relative to water column frP) and the potential sorption sites ($S_{max} - S_0$), the bed sediments in the UBR are capable of removing much more $PO_4^{3-}$ than is exported from the river system on an annual basis. However, during event flows the potential for exchanges of $PO_4^{3-}$ across the sediment–water interface is limited due to the high flow velocities. Therefore, the greatest potential for adsorption at high flow is with suspended sediments entrained from the streambed. However, the extent to which resuspended sediments buffer water column frP appears to be limited based on a comparison of sediment $EPC_0$ and event flow frP in the UBR. If resuspended bed sediments controlled event flow frP in the UBR then event flow concentrations should be lower. This was not the case indicating that $PO_4^{3-}$ fluxes at high flow are determined by the properties of the soils. Therefore, a combination of high inputs from surface soils, and limited adsorption by suspended sediments, results in substantial export of $PO_4^{3-}$ from the river system during large storm events. This could help to explain why the majority of annual frP export from the UBR occurs during flow events (Kerr 2009).

In contrast to the UBR, McDowell and Sharpley (2001) found that streambank soils had lower $EPC_0$

relative to bed sediments from an agricultural catchment in central Pennsylvania, USA. The degree of variability in $EPC_0$ between soils and sediments was small compared to the UBR catchment. Likewise, in a mixed land use catchment in Scotland, Stutter and Lumsdon (2008) reported similar $EPC_0$ values for river sediments and soils. There is likely to be less variation in water column $PO_4^{3-}$ under high and low flows in these systems because there is less variation in $EPC_0$ between soil and sediment pools. The exception in our study was Emu Ck, where there was less variation in $EPC_0$ and $NH_4Cl$–P between soil and sediment pools and also less variation in frP between high and low flows. It could be argued that the lower variation between event and baseflow frP at Emu Ck was due to less variation in $NH_4Cl$–P and $EPC_0$ between soils and sediments.

$Fe_{ox}$ is likely to have a substantial effect on P sorption across terrestrial and aquatic components of the catchment. $Fe_{ox}$ was clearly much higher in sediments relative to soils despite similar % fines, and LOI, $Al_{ox}$ and NAIP concentrations. The fact that none of these parameters was higher in sediments relative to soils suggests that the elevated $Fe_{ox}$ was not due to preferential erosion and deposition of $Fe_{ox}$ in bed sediments. Therefore, it is likely that the increased $Fe_{ox}$ in bed sediments was the result of in-stream processes. Sah et al. (1989b) compared Fe speciation in soils before and after flooding and found that amorphous Fe increased at the expense of free Fe oxides as flooding period increased. Furthermore, flooding increased P sorption by 10–70% in half of the ten soils measured (Sah et al. 1989a). More recently, Zhang et al. (2003) found that soil flooding significantly increased amorphous Fe, mainly at the expense of more crystalline forms in paddy soils of southeast China. Again, flooding increased P adsorption and maximum P adsorption capacity. A similar process may have occurred in the UBR catchment. As soils in the UBR are eroded and deposited as sediments, there is an increase in amorphous Fe at the expense of crystalline forms. It is suggested that this increases P adsorption and reduces $EPC_0$ and $NH_4Cl$–P. This in turn has a substantial affect on $PO_4^{3-}$ exchanges at the catchment scale.

It should be noted that the pattern of $EPC_0$ and $Fe_{ox}$ in soils and sediments at Emu Ck was opposite to what was observed at the UBR sites. This may have been a reflection of the different underlying geology at this site, although this is difficult to ascertain as this was the only site located within the Maronghi Creek Bed formation. Differences in flow characteristics between Emu Ck and the UBR may have also been important. The relatively low proportion of fine sediments at Emu Ck probably reflects a higher flow velocity at this reach relative to the UBR. This may have reduced the overall P sorption capacity of the bed sediments at Emu Ck relative to the source material. While the importance of this process is difficult to interpret from our results, further investigation into the relationship between flow, transport and deposition of fine sediments, and P sorption is warranted as this may be an important source of variation in P sorption between different reaches.

The UBR catchment is a degraded system with evidence of hillslope and gully erosion, particularly in areas where grazing occurs. This would exacerbate $PO_4^{3-}$ desorption from soils during rain events. The high exchange of $PO_4^{3-}$ during rain events has important implications downstream. The UBR flows into a large water reservoir, Wivenhoe reservoir, a phosphorus limited system (Burford and O'Donohue 2006). There is evidence for increased $PO_4^{3-}$ concentrations during inflow events and a subsequent rapid increase in cyanobacterial cell densities (M. Burford, unpubl. Data). This reservoir has a toxic cyanobacterium *Cylindrospermopsis* as a dominant species and water managers spend considerable resources monitoring this species and its toxins, and treating water. Based on the results of this study, it would appear that management strategies focussed at reducing erosion and increasing pasture and forest cover at a whole-of-catchment scale will be most effective at reducing $PO_4^{3-}$ losses, and the subsequent water quality problems downstream.

## Conclusion

Our study has shown that sorption and exchangeable P differed substantially between soils and sediments. These differences appeared to be due to an increase in amorphous Fe when soils are deposited and processed within the river system. Due to a large sorption gradient between soils and sediments, the UBR system is characterized by extremes of movement into and out of the soil/sediment system during periods of high and low flow. The UBR catchment has poor $PO_4^{3-}$ retention capacity during rain events. This is largely due to increased hydrological connectivity between loosely sorbed P in the soils, and the river system. The greatest potential for retention is at low flow and is likely to be via the riverbed sediments. Therefore, the river system plays an important role in reducing the flux of $PO_4^{3-}$ to downstream ecosystems, while processes occurring in the soils are the principle source of $PO_4^{3-}$ export from the system.

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