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Changyou Wang

Nanjing University of Information Science and Technology, changyou@uow.edu.au

R John Morrison

University of Wollongong, johnm@uow.edu.au

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Phosphorus speciation and changes with depth in the sediment of Lake Illawarra, New South Wales, Australia

Abstract

In order to better understand phosphorus (P) cycling and origins in the sediment of the Lake Illawarra, two sediment cores were extracted in November, 2010 and a modified sequential extraction scheme (SEDEX) was used to profile the exchangeable P (Pex), reactive Fe/Al-bound P (Preac), reductive Fe/Al-bound P (Predu), authigenic apatite P (Pauth), detrital P (Pdet), organic P (Porg) and residual P (Presi). The total sedimentary P (TP) ranged from 93 to 437 $\mu\text{g g}^{-1}$, and was dominated by inorganic P. The average percentage of each fraction of P in the sediment followed the sequence: Preac (28.6 %) > Presi (23.5 %) > Pauth (19.1 %) > Predu (17.0 %) > Porg (4.9 %) > Pex (4.7 %) > Pdet (2.2 %). The profiles of TP and Porg showed two peak values with depth, which were matched to land use history in the Lake Illawarra catchment. The sediment depth profiles indicated that Fe oxyhydroxides play a predominant role in the P cycle in the sediments of the lagoon. This is supported by significant positive correlation between Preac and reactive Fe and a negative correlation between Pauth and Fe. Pauth and Preac concentrations were also well negatively correlated, possibly a result of competitive equilibrium between Fe and Ca for P. The estimated P burial efficiency was up to 82 % for this lagoon, which is likely related to the high sediment accumulation rate and the high value of R Fe-P. In addition, the bioavailable P, which consists of Pex, Preac, and Porg, represented a significant proportion of the sedimentary P pool, accounting, on average, for 38 % of the TP. This result indicates that the sediment is a potential internal source of P for this lake ecosystem.

Keywords

Phosphorus, Speciation, Sediment, Lake Illawarra

Disciplines

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Phosphorus speciation and changes with depth in the sediment of Lake Illawarra, New South Wales, Australia

Changyou Wang^a, R. John Morrison^{b*}

a. School of Marine Sciences, Nanjing University of Information Science and Technology, Nanjing 210044, China

b. School of Earth and Environmental Sciences, University of Wollongong, NSW 2522, Australia

Abstract: In order to better understand phosphorus (P) cycling and origins in the sediment of the Lake Illawarra, two sediment cores were extracted in November, 2010 and a modified sequential extraction scheme (SEDEX) was used to profile the exchangeable P (P_{ex}), reactive Fe/Al bound P (P_{reac}), reductive Fe/Al bound P (P_{redu}), authigenic apatite P (P_{auth}), detrital P (P_{det}), organic P (P_{org}) and residual P (P_{resi}). The total sedimentary P (TP) ranged from 93 to 437 $\mu\text{g g}^{-1}$, and was dominated by inorganic P. The average percentage of each fraction of P in the sediment followed the sequence: P_{reac} (28.6%) > P_{resi} (23.5%) > P_{auth} (19.1%) > P_{redu} (17.0%) > P_{org} (4.9%) > P_{ex} (4.7%) > P_{det} (2.2%). The profiles of TP and P_{org} showed two peak values with depth, which were matched to land use history in the Lake Illawarra catchment. The sediment depth profiles indicated that Fe oxyhydroxides play a predominant role in the P cycle in the sediments of the lagoon. This is supported by significant positive correlation between P_{reac} and reactive Fe and a negative correlation between P_{auth} and Fe. P_{auth} and P_{reac} concentrations were also well negatively correlated, possibly a result of competitive equilibrium between Fe and Ca for P. The estimated P burial efficiency was up to 82% for this lagoon, which is likely related to the high sediment accumulation rate and the high value of R_{Fe-P} . In addition, the bioavailable P, which consists of P_{ex} , P_{reac} , and P_{org} , represented a significant proportion of the sedimentary P pool, accounting, on average, for 38% of the TP. This result indicates that the sediment is a potential internal source of P for this lake ecosystem.

Key Words: Phosphorus, speciation, sediment, Lake Illawarra

1. Introduction

Phosphorus (P) is intimately involved in both terrestrial and marine biogeochemical cycles (Blake et al. 2005; Jaisi and Blake 2010) and plays a key role in determining the ecological status of aquatic systems. P is a potentially limiting nutrient that sustains primary productivity and has been recognized as a key factor responsible for eutrophication in lagoon, estuarine and other marine waters (Anschutz et al. 2007; Hou et al. 2009). The magnitude of primary production depends on the content of phosphorus bioavailable to autotrophic organisms in these coastal areas (Monbet et al. 2007a; Wang et al. 2009). Weathering, field runoff and anthropogenic sewage effluent are the primary agents for mobilizing P from continental sources, and rivers are the primary carriers of P to the estuary waters, coastal lagoons and oceans (Compton et al. 2000; Withers et al. 2009). In shallow aquatic systems, P is removed predominantly by primary production. However, most of the freshly deposited organic matter is decomposed, and P is rapidly remineralized and released to the

sediment pore water from which it can readily escape to the overlying water (Anschutz et al. 2007). Depending on the environmental conditions, this released P may be also adsorbed to particle surfaces, co-precipitated with iron and aluminium oxyhydroxides, or eventually transformed to authigenic mineral carbonate fluorapatite within the sediments (Monbet et al. 2007a; Jaisi and Blake 2010). These processes are interrelated, e.g., Fe-bound P may act as an intermediate between organic P and apatite P (Slomp et al. 1996). Only a portion of the particulate phosphorus that reaches the sediment-water interface is actually buried with the accumulating sediment (Sundby et al. 1992; Compton et al. 2000; Anschutz et al. 2007). As burial in sediments usually represents the only sink for P in the aquatic environment, it is of primary importance to characterize the P speciation and changes with depth if considering the sedimentary P origin.

As an enclosed, saline, coastal lagoon, with very limited tidal exchange and almost entirely surrounded by residential development, Lake Illawarra had been subjected to continuous urban pollution (Yassini and Jones 1987; Clarke and Dooley 2004) for over 100 years. Environmental issues and rapid sedimentation are recognised problems in the lake (Gillis and Birch 2006; Rutten 2007). The very high sediment P levels is a major concern. Several studies have reported P concentrations in the inorganic, organic or phosphine pools in the sediments, trying to evaluate the importance of the P cycling in the sediment of the Lake Illawarra (Rutten 2007; Song et al. 2011). However, seldom has attention been paid to P speciation and the changes in the sediments, nor the P origin and the relationship between changes in P speciation and environmental conditions. In this context, this study aimed to determine the P speciation and changes with depth in the sediment of the Lake Illawarra, helping to understand the P sedimentation history and identify the potential risk of P in this lake ecosystem.

2. Materials and Methods

2.1 Description of Lake Illawarra

Lake Illawarra (Figure 1) is a coastal lagoon, located 80 km south of Sydney, New South Wales (34°32'S, 150°50'E). It is a shallow, elongated waterbody, oriented in a north-east to southwest direction, being 9.5 km long, 5.5 km wide and up to 3.7 m (average 1.9 m) deep, with a surface area of 35 km² (Chenhall et al. 1994). The catchment area is about 235 km², comprising 23% suburbs and industry, 37% native vegetation and 40% rural land (Gillis and Birch 2006). The average yearly water input of the lagoon is about 80×10^6 m³, of which Macquarie Rivulet provides an annual average of 42×10^6 m³ and the rest is contributed by rainfall and other smaller creeks. The annual average rainfall in the catchment of the lagoon varies from 1600 mm in the west to 1130 mm adjacent to the shoreline (Yassini and Jones 1987). The lagoon was formed 6000-6500 years ago, by the formation of a sand barrier across the eastern side of a shallow embayment and subsequent flooding of the adjacent river plain. Today the lagoon is separated from the ocean by a tidal channel 2.4 km long, approximately 600 m wide and 2.0-3.5 m deep, with attenuated tides of 0.2 m in the entrance channel and <0.1 m in the central lake (Yassini and Jones 1987; Gillis and Birch 2006). On several occasions in the last 70 years, heavy shoaling at the mouth has resulted in the complete closure of the lagoon. Such events occurred most recently from 1995 to 2007 with the entrance closed on average about 20% of the time (Yassini and Jones 1987; Song et al. 2011). Until 2007, the average tidal charge (flood and ebb tide) and discharge was in the order of 0.5×10^6 m³ with the residence time of the lagoon water mass varying between approximately 180 and 270 days (Ellis et

al. 1977). However, training walls were constructed on both sides of the entrance channel between 1998 and 2007 such that the lake flushing time for different entrance conditions is now estimated to be less than 50 days (Clarke and Dooley 2004).

2.2 Sample collection and treatment

Samples of sediments were collected at 34° 32' 3" S, 150° 50' 31" E and 34° 32' 0" S, 150° 50' 13" E with water depths of 1.2 m and 2.9m, respectively, in the Lake Illawarra (Figure 1) on November 17, 2010. The sediment core was collected with aluminum alloy tubes (300 cm long and 10 cm wide), which were inserted directly into the sediment with a vibracorer. When the tube went about 100-130 cm into the sediment, the motor was stopped and the core was withdrawn from the surrounding sediment and sealed with the plastic caps and tape. Care was taken to preserve sediment structure during sampling and transportation to the laboratory. The sediment cores sample were stored in a cool room under 4°C until cores sectioning were carried out. The cores were sectioned into 7 layers as described in Tables 1 and 2 (thickness according to the content of silt and shells). The separated sediment samples were air-dried at room temperature and ground to <250 µm. The pH in the Lake Illawarra sediment were steady basically and consistent with the literatures (Sloss 2005; Chenhall et al. 1995), ranging from 7.6-8.0.

Fig. 1 Map showing the location of Lake Illawarra and coring sites

2.3 Solid-phase analysis

Sediment P speciation was obtained using a SEDEX sequential extraction procedure slightly modified from Ruttenberg (1992). The sedimentary P pools separated by this technique are (1) exchangeable or loosely adsorbed P (P_{ex}) extracted with 1 M $MgCl_2$, (2) reactive Fe/Al bound P (P_{reac}) extracted with 1 M NaOH, (3) reductive Fe/Al bound P (P_{redu}) extracted with CDB (0.3 M $Na_3C_6H_5O_7 \cdot 2H_2O$ + 1 M $NaHCO_3$ + 1.125g $Na_2S_2O_4$), (4) authigenic apatite plus $CaCO_3$ -bound P plus biogenic apatite (P_{auth}) extracted with 1 M HAc-NaAc, (5) detrital apatite of igneous or metamorphic origin (P_{det}) extracted with 1 M HCl, (6) organic P (P_{org}) extracted with 1 M HCl after Calcination 550°C and (7) residual phosphorus (P_{resi}) determined by XRF. The 0.5 g of dry and ground sediment sample was extracted with 50 ml extractant. There were only two modifications to the original SEDEX protocol. First, reactive Fe/Al bound P was determined using 1.0 M NaOH

recommended by Kerr et al. (2010), Ruban et al. (1999, 2001) and Pettersson et al. (1988). The extraction procedure of Ruttenberg offers a means for separating authigenic carbonate fluorapatite from detrital apatite of igneous or metamorphic origin, but it is not sufficient for separation of other P speciations. For example, the P extracted with CDB includes not only the reductive Fe-bound P, but the reactive Fe/Al-bound P which was considered as bio-available and extracted with NaOH (Ruban et al. 1999, 2001). Second, the residue in second step was washed using 1 M NaCl instead of 1M MgCl_2 in order to avoid $\text{Mg}(\text{OH})_2$ precipitation.

All phosphate concentrations in the extracted supernatants were determined with the phosphomolybdate blue method (Murphy and Riley 1962). Prior to analysis, all leachates were diluted in de-ionised water and phosphate extracted from the sediments was measured using a UV-Visible-Spectrophotometer (UV 1700, Shimadzu Co., Japan) with a detection limit of 0.02 μM . Precision based on replicate analyses was generally less than 7%. The reference material (EMAI/PIT/98, <250 μm , TP 1140-1220 $\mu\text{g g}^{-1}$), provided by School of the Earth and Environmental Sciences, University of Wollongong, was also sequentially fractionated and analyzed to check the analytical quality. Average relative error of TP in the reference material was less than 10%. In addition, replica analysis of three sediment samples led to average coefficients of variance of 11, 5, 7, 24, 1 and 7% for P_{ex} , P_{reac} , P_{redu} , P_{auth} , P_{det} and P_{org} respectively. The P_{resi} contents were determined by X-Ray Fluorescence (Ametak SpectroXEPOS) (Ismail et al. 2010). Total phosphorus was determined by the sum of all the speciation fractions and the residual P. Al, Fe and Ca were also determined by X-Ray Fluorescence (Ismail et al. 2010). Active Fe was estimated from the difference in Fe concentration determined by XRF before and after sequential extraction. Average analytical precision was 10% for these elements. All reagents were analytical grade.

3. Results and discussion

3.1 Phosphorus speciation and changes with depth

Depth profiles of sediment cores TP and sequentially extracted sedimentary P fractions are shown in Figures 2 and 3. TP concentrations ranged from 312 to 437 $\mu\text{g g}^{-1}$ in core B and from 92 to 156 $\mu\text{g g}^{-1}$ in core C, and both showed two peak values with depth. The increase was much more pronounced from the third to fifth layers in the core. However, TP decreased with depth in the last 3 layers.

The best dating information for cores in the area of our core was by Sloss (2005) who looked at about 20 cores from Lake Illawarra to try and understand the sedimentation history. One of his cores and the cores from this study were located close together, and the best evidence from these showed that a core of 1 metre depth in this area of the lake corresponds to about 190 years before 2010 (that is, about 1820), indicating an average sedimentation rate of 5.2 to 5.3 mm a^{-1} . Based on this sedimentation rate, the period dated by depth of sediment layer was estimated as listed in Tables 1 and 2. As it is well known that weathering, field runoff and urban wastewater are the primary agents for P from continental sources, the information on land use history in the Lake Illawarra catchment can be matched to the P data in a reasonable way.

Significant areas of land within the Lake Illawarra catchment were cleared initially for agricultural purposes followed by dairy farming during the 1800s. Cedar cutters in the early 1800s were the first-known Europeans to impact the catchment. Agricultural production, primarily wheat, oats and potatoes, commenced in 1816 with the surveying and clearing of large land grants

surrounding the lake foreshore (Lake Illawarra Authority 2012). Between late 1816, when the first land grants were marked out, and the mid-1800s, land clearing occurred slowly (Hopley et al. 2007). This process expanded rapidly thereafter. Crops such as wheat, oats and potatoes were grown around the lake and dairying became the primary industry in the late 1880s (Lake Illawarra Authority 2012). Assuming that the amount of fertilizers applied per acre in the cultivated fields were basically constant, the phosphorus content in sediments produced by soil erosion, through river to coastal water bodies, should be proportional to the area of cultivated fields. This period with increase in land clearing for agricultural purposes possibly corresponded to the 60-100 cm layers in the core B with the maximum TP in the 60-73 cm layer, and to the 61-110 cm layers in the core C with the maximum TP in the 61-85 cm layer. Dairy farming and pasture improvement replaced crop production in the late 1800s, which was possibly the reason for a decrease in the TP value in the 48-60 cm layer of the sediment core B and in the 47-61 cm layer of the sediment core C. By the late 1920 – 1930s, the focus on land clearing had ceased, with many farmers now concerned with pasture improvement as dairy farming replaced crop production (Hopley et al. 2007), probably indicating the lower extremum value in the 31-48 cm layer of the sediment core B and in the 27-47 cm layer of the sediment core C.

As areas around the Lake became more accessible, the population began to expand rapidly from the 1950s (Campbell 2004). Significant urban development appears to have commenced in the 1960s based on an analysis of aerial photographs (Hopley et al. 2007). The population within the Lake catchment increased from around 5,000 in 1950 to around 90,000 in 2003. This significant increase in population growth, combined with runoff from agricultural activities in the catchment, has placed extreme pressure on the environmental health of the Lake. It was not until the early 1980s that all areas around the lake shoreline were sewered, and problems with the Lake started to manifest themselves in the 1970s, when large algal blooms started to frequently occur (Campbell 2004). It is likely that the urban expansion is responsible for the higher TP value in the 13-31 cm layer of the sediment core B and in the 7-27 cm layer of the sediment core C.

The environmental problems of Lake Illawarra were so serious that the New South Wales State Government considered them to be a major regional priority. The Lake Illawarra Authority was established in February 1988 with the task of repairing the damage that had occurred to the Lake and its foreshores over the previous 150 years. Many solutions to the human environmental impacts upon Lake Illawarra have been proposed in recent years and some have been implemented (Campbell 2004). The effect of these solutions was well represented with the decrease in TP concentration in sediment to a minimum value for the core in the 0-13 cm layer of the sediment core B and in the 0-7 cm layer of the sediment core C. The coincidence between the dated periods and the land use in the catchment also serves as a supporting evidence for the lake sedimentation rate used.

Table 1 The selected characteristics and the dated periods of the core B sediment in the Lake Illawarra and the typical land use in its catchment

Depth (cm)	Descriptions	Periods dated by depth	Typical land use in the catchment
0-13	very well silt with minimal shell and reasonable sharp contact	2010-1985	repairing the damage that had occurred to the Lake
13-31	shell rich silt layer	1985-1951	significant urban development
31-48	shell rich silt layer	1951-1919	the focus on land clearing had ceased
48-60	shell poor silt layer	1919-1896	dairy farming and pasture

			improvement replaced crop production
60-73	shell poor silt layer	1896-1871	crops were grown around the lake catchment
73-84	shell rich silt layer	1871-1850	continued land clearing occurred rapidly
84-100	relatively shell poor silt layer	1850-1820	initial land clearing occurred slowly

Table 2 The selected characteristics and the dated periods of the core C sediment in the Lake Illawarra and the typical land use in its catchment

Depth (cm)	Descriptions	Periods dated by depth	Typical land use in the catchment
0-7	sand and silt with several minimal shell and reasonable sharp contact	2010-1997	repairing the damage that had occurred to the Lake
7-27	shell rich sand and silt layer	1997-1958	significant urban development
27-47	shell rich sand and silt layer	1958-1920	the focus on land clearing had ceased
47-61	shell poor sand and silt layer	1920-1894	dairy farming and pasture improvement replaced crop production
61-85	shell rich sand and silt layer	1894-1848	crops were grown around the lake catchment ← continued land clearing occurred rapidly
85-110	shell poor sand and silt layer	1848-1800	initial land clearing occurred slowly
110-129	relatively shell rich sand and silt layer	1800-1764	virgin soil

Fig. 2 Solid-phase profiles of P (μg g⁻¹) as determined with the extraction procedure: P_{ex}, P_{reac}, P_{redu}, P_{auth}, P_{det}, P_{org}, P_{resi} and TP for the core B sediment sampled in Lake Illawarra.

Fig. 3 Solid-phase profiles of P ($\mu\text{g g}^{-1}$) as determined with the extraction procedure: P_{ex} , P_{reac} , P_{redu} , P_{auth} , P_{det} , P_{org} , P_{resi} and TP for the core C sediment sampled in Lake Illawarra.

Exchangeable or loosely sorbed P

The P_{ex} concentrations were $<26 \mu\text{g g}^{-1}$ in the Lake Illawarra and usually represented $<8\%$ of TP. Variations in P_{ex} concentrations with depth were generally small. Moreover, P_{ex} and Fe depth profiles were relatively well mirrored (Fig. 2, Fig. 3, Fig. 4 and Fig. 5). This is usually attributed to a result of the reduction of Fe oxides related to the redox condition and intensity (Monbet et al. 2007b) and suggests that Fe in core sediment may control the depth profile of the P_{ex} .

Fig. 4 Depth profile of Fe, active Fe, Al and Ca in the core B sediment of the Lake Illawarra

Fig. 5 Depth profile of Fe, active Fe, Al and Ca in the core C sediment of the Lake Illawarra

Reactive Fe/Al bound-P

P_{reac} is considered as the fraction associated with Al, Fe and Mn oxyhydroxides (Ruban et al. 1999). In this lagoon, P_{reac} concentrations ranged from 25 to 172 $\mu\text{g g}^{-1}$, which always represented a major proportion of the TP pool (up to 17-40% of TP). The depth profile of P_{reac} was characterised by a maximum concentration in 60-73 cm layer in core B sediment and in 110-129 cm layer in core C sediment. This pattern is different from the usual profile dominated by redox conditions, which presents a maximum concentration in surface sediment, followed by a decrease with depth down to a relatively constant value (Dai et al. 2006; Monbet et al. 2007a). In addition, P_{reac} and Fe /Al concentrations were positively correlated (for core B: Fe $r=0.74$, $n=7$, $P<0.05$, Al $r=0.84$, $n=7$, $P<0.01$; for core C: Fe $r=0.81$, $n=7$, $P<0.05$, Al $r=0.7$, $n=7$, $P<0.1$).

Phosphorus and iron are often bound in sediments. P is adsorbed on iron complexes by ligand exchange (Ruban et al. 1999). Particulate Fe in sediment usually occurs as Fe oxyhydroxide (FeOOH) or siderite (FeCO₃), pyrite (FeS₂), iron monosulfides (FeS) and vivianite (Fe₃(PO₄)₂·8H₂O) or bound in aluminium silicates (Burdige 1993). The amounts of FeOOH, the poorly crystalline ferrihydrite and akaganeite play a dominant role for binding P in sediment and are the factors controlling P release from the sediment (Slomp et al. 1996; Ruban et al. 1999). This is consistent with our observation which demonstrated the interactions between phosphate and active Fe are a principal mechanism for the changes of P_{reac} with depth profile. There is also a significant positive correlation between P_{reac} and active Fe (for core B: $r=0.97$, $n=7$, $P<0.0002$; for core C: $r=0.87$, $n=7$, $P<0.01$) (Fig. 6).

Fig. 6 Relationships between P_{reac} and active Fe in core B (left) and core C (right)

The Fe:P ratio is considered to be a measure of free sorption sites for phosphate ions on iron oxyhydroxide surfaces (Jensen et al. 1992; Jensen and Thamdrup 1993; Coelho et al. 2004). The lower Fe:P ratios suggest saturation of sorption sites or less capacity to adsorb phosphate, resulting

in phosphate efflux to the overlying water. It has been found that sediments with molar Fe:P ratios above 8.5 in fresh water or 13.7 in saline water were capable of retaining phosphate in the oxidized surface layer otherwise phosphate would leach (Jensen et al. 1992; Coelho et al. 2004). For the sediments of the Gippsland lakes, Victoria, Australia, this ratio was about 40–125 in summer and most of the P derived from primary production was temporarily retained in the sediment (Monbet et al. 2007a). The molar ratio of total Fe to P_{reac} was 36–313 in the sediment of Lake Illawarra (Table 3). This may suggest that Fe oxyhydroxides in the sediments of Lake Illawarra might be able to sequester more phosphorus. The observations above showed that Fe oxyhydroxides play a dominant role in the P cycle in the sediment of this lagoon.

Table 3 Molar ratios of Fe to P_{reac} and Ca to P_{auth} in the sediment of core B and C in the Lake Illawarra

Core B				Core C			
Depth (cm)	Fe : P_{reac}	Active Fe : P_{reac}	Ca : P_{auth}	Depth (cm)	Fe : P_{reac}	Active Fe : P_{reac}	Ca : P_{auth}
0-13	220	93	1055	0-7	46	39	135
13-31	258	106	619	7-27	40	34	41
31-48	266	100	1087	27-47	49	41	70
48-60	187	96	144	47-61	57	46	132
60-73	154	86	144	61-85	49	41	357
73-84	299	93	1053	85-110	40	34	33
84-100	313	113	647	110-129	36	31	104

Reductive Fe/Al bound-P

P_{redu} , which is considered as Fe/Al-phosphates coated with iron oxyhydroxides and carried by streams from catchment weathering origins (Petersen and Corey 1966; Nguyen 2000), ranged from 7 to 38 $\mu\text{g g}^{-1}$, represented 2-9% of TP in the core B sediment and 25-38% of TP in the core C. The P_{redu} concentrations remained relatively constant in the first 5 layers in core B, below which concentrations increased dramatically with depth, while P_{redu} increased slowly with depth in core C. The increase with depth here was associated with a concomitant increase of detrital apatite P concentration, most likely an outcome of the same terrigenous origin as detrital apatite P in the catchment (Fig 2 and Fig 3).

Authigenic P and detrital P

P_{auth} usually occurs as authigenic carbonate fluorapatite, biogenic apatite or CaCO_3 -associated P in the sediment (Ruttenberg 1992). The P_{auth} concentrations were high, as expected from the relatively high content of Ca in the sediments. They ranged from 21 to 66 $\mu\text{g g}^{-1}$ and represented 10-28% of TP in the sediment samples. There was obvious variation in P_{auth} concentration with depth. The decrease in P_{auth} concentrations was associated with a concomitant decrease of shell content in the sediment, especially pronounced in the 48-60 cm layer in the core B and the 47-61 cm layer in the core C, which may suggest that P_{auth} in this lagoon is of a pronounced biogenic origin. P_{auth} and P_{reac} depth profiles were relatively well mirrored, with a significant negative correlation (for core B: $r = -0.84$, $n=7$, $P < 0.02$; for core C: $r = -0.5$, $n=7$, $P < 0.2$). This pattern might relate to the vertical variations of P_{org} , Fe and Ca in the core sediment (Fig. 2, Fig. 3, Fig. 4 and Fig. 5). During early diagenetic reactions, the P released from organic P degradation may be captured via authigenic

carbonate fluorapatite formation and Fe/Mn oxyhydroxides (Filippelli and Delaney 1996; Katsaounos et al. 2007; Hou et al. 2009). However, owing to the presence of substantial amounts of Fe oxyhydroxides, competition equilibrium occurred between Fe and Ca (Ruttenberg and Berner 1993; Lucotte et al. 1994; Monbet et al. 2007b; Lillebø et al. 2012). So P_{auth} decrease can be attributed to the competition of substantial amounts of Fe with Ca for phosphate in sediment. This mechanism is supported by a significant positive correlation between P_{auth} and Ca (for core B: $r = 0.81$, $n=7$, $P < 0.05$; for core C: $r = 0.75$, $n=7$, $P < 0.05$) and a negative correlation between P_{auth} and Fe (for core B: $r = -0.75$, $n=7$, $P < 0.05$; for core C: $r = -0.5$, $n=7$, $P < 0.2$). These results also indicate that P geochemistry appeared to be controlled mainly by Fe in this lagoon, which is consistent with the Gippsland Lakes, another coastal lagoon in Victoria, Australia (Monbet et al. 2007a).

P_{det} , which includes P bound to apatite from igneous and metamorphic origin and is carried by streams, was very low, ranging from 0.7 to $22\mu\text{g g}^{-1}$. Depth profiles basically showed an increase with depth. P_{det} rarely exceeded 5% of TP and constituted the lowest fraction of the TP pool.

Organic P

P_{org} showed large variations in concentration in Lake Illawarra, ranged from 1 to $45\mu\text{g g}^{-1}$ and represented 1-10% of TP. Depth profiles of P_{org} showed two peak values with depth, similar to that of TP. The increase was obvious between the third and fifth layers in the core B and C, and the decrease from the fifth to the seventh sediment layers was much more pronounced.

The depth profile of P_{org} in this lagoon sediment is different from the usual profile of stable deposition, which presents a maximum concentration in the surface sediment, followed by a decrease down to a relatively constant value with depth (Berner 1980). This indicated that the accumulation rate of P_{org} varied continually with time over the past 200 years in this lagoon, especially in the late 1800s. Considering also the similar changing trend with time in TP concentration, an increase in P inputs would be presumed in the late 1800s, which certainly served to increase the primary productivity loop and then the export of organic P to the sediment. Also the decomposition of the excess organic matter would reduce dissolved oxygen in bottom water, resulting in hypoxia and a decrease in numbers of benthic species. This inference coincided with the shell observations in the sediment core. The two peak values in P_{org} concentration with depth were likely to reflect the enhanced flux of organic matter burial in the sediment with P and are explained principally by the land use in the catchment, which corresponded to large scale agricultural activities and urban development, respectively. Since P_{org} is better than TP when used as the indicator for eutrophication (Vaalgamaa 2004; Dai et al. 2006), the decrease in P_{org} concentration reflects the improved environmental quality in Lake Illawarra.

Compared with high P_{reac} and P_{auth} , the relatively low P_{org} is likely to be a result of rapid organic matter decomposition reactions that released orthophosphate into pore waters to be captured via Fe oxyhydroxides or authigenic carbonate fluorapatite formation.

Residual phosphorus

P_{resi} showed large variations in concentration, ranging from 6 to $186\mu\text{g g}^{-1}$ and representing 5 - 44% of TP. The XRF showed that the residue after extraction were mainly formed by Na_2O , MgO , Al_2O_3 , SiO_2 , P_2O_5 , SO_3 , K_2O , CaO , TiO_2 , MnO , Fe_2O_3 , with average mass percentage of 5.05, 1.59, 14.12, 41.38, 0.13, 3.61, 1.72, 7.73, 0.73, 0.05 and 6.18%, respectively. Depth profiles showed a peak values with depth, with the maximal P_{resi} concentrations in the 73-84 cm layer in the core B and

the 61-85cm layer in the core C.

3.2 Post-depositional reorganisation and bioavailable P fraction

Post depositional reorganisation processes are important because they ultimately control the amount of P buried in the sediment. A quantitative assessment of the amount of P released by the different sedimentary forms of P has been carried out using a trapezoid integration of the depth profiles and the results are shown in Table 4. P_{det} and P_{resi} were excluded from this calculation because they are believed to be un-reactive in nature. Depth integrated P_{reac} , P_{org} , P_{redu} and P_{ex} were characterised by a gain of P. The gain in P_{org} did not result from a transfer of P from other species but from a difference in accumulation rate of P_{org} with time, which could be supported by the land use in the catchment and the high accumulation rate (see Table 1 and parts 3.3). P produced by organic matter decomposition would appear to be redistributed in favour of P_{reac} by adsorption onto iron oxyhydroxides (Monbet et al. 2007b). These results are also indicative of the large capacity of the sediment to sequester P within Lake Illawarra, which is also supported by the burial efficiency of phosphorus calculated in this study (see part 3.3). Even so, the release of P_{reac} is expected under conditions of bottom water hypoxia. Only the integrated P_{auth} indicated a minor loss of P. As explained above, the loss in P_{auth} did not result from apatite dissolution, but more likely from a difference in source material over time.

Table 4 Depth integrated changes (over 0-100 cm for the core B and 0-129 cm for the core C) in sediment P species (negative values represent P loss, and positive values represent P gain, compared with P concentration in the first layer)

	Integrated variation ($\mu\text{g cm}^{-2}$)				
	P_{ex}	P_{reac}	P_{redu}	P_{auth}	P_{org}
Core B	328.3	1327.9	345.9	-153.3	988.5
Core C	286.8	1380.7	1227.3	-1736.7	80.8

Eutrophication may continue to occur long after phosphorus inputs have ceased due to remobilization of phosphorus bound to sediments (Monbet et al. 2007a). Changes of physical, chemical, and biological conditions can induce release and transformation of phosphorus from the sediments (Anschutz et al. 2007; Kerr et al. 2010). The released phosphorus is available for algal growth and can further sustain the eutrophication processes (Coelho et al. 2004). Generally, bioavailable or mobile phosphorus in the sediment can be defined as the sum of immediately available phosphorus and potential phosphorus that can be transformed into an available form by naturally occurring physical, chemical and biological processes (Wang et al. 2009). Bioassays indicate that the P_{ex} is available for algal growth. The P_{reac} is potentially bioavailable, depending primarily on sediment redox intensity (Katsaounos et al. 2007). In algal bloom areas of this lagoon, characterized by deficiency in nocturnal dissolved oxygen concentration, P_{reac} can intermittently be reduced and released from sediments into the water column (Yassini and Jones 1987; Jensen and Thamdrup 1993; Hou et al. 2009). P_{org} could become bioavailable by microbial remineralization. However, P_{redu} hardly becomes bioavailable unless very strong sediment redox intensity occurred (Li et al. 1998). The P_{auth} and P_{det} are almost insoluble in coastal waters and believed to be less available for organisms (Coelho et al. 2004). P_{resi} is unreactive even in strong acidic and alkaline

solution. Therefore, only the P_{ex} , P_{reac} and P_{org} should be considered as potentially bioavailable in the Lake Illawarra ecosystem. Figure 7 shows the depth profile of bioavailable P in the sediment core studied. The bioavailable P concentration ranged from 28 to 240 $\mu\text{g g}^{-1}$, representing 26 to 55% of the TP.

Fig. 7 Depth profile of the bioavailable P in the core B sediment (left) and the core C sediment (right) from the Lake Illawarra.

The bioavailable P concentrations varied significantly with depth. The profile pattern for the core B, characterised by a peak concentration in 60-73 cm layer, was different from that for the core C. This should result from the difference in depth profile of the active Fe between the core B and the core C (Fig. 4 and Fig. 5), which also showed a peak concentration in 60-73 cm layer in the core B. As P_{reac} represented 60-90% of the bioavailable P and the interactions between phosphate and active Fe are a principal mechanism for the changes of P_{reac} with depth profile, there is also a significant positive correlation between the bioavailable P and active Fe (for core B: $r = 0.97$, $n=7$, $P < 0.0004$; for core C: $r = 0.85$, $n=7$, $P < 0.01$). Compared with the sediments from the Gippsland lakes (Monbet et al. 2007a), bioavailable P was relatively higher in this lake. This indicates that the sediment is an important internal source of P for the Lake Illawarra ecosystem. However, further study is needed to quantitatively elucidate the coupling relationship between sedimentary P cycling and aquatic ecosystem processes in the study area.

3.3 Sedimentation and burial efficiency of phosphorus

Phosphorus accumulation in sediment can be estimated by sedimentation rate, bulk density and P concentration. The average sedimentation rates have been inferred above to be 5.25 mm a^{-1} and the sediment bulk density reported for Lake Illawarra is 1.3 g cm^{-3} (Yassini 1994). In this case, the estimated mass accumulation rate of sediment (MAR) from sedimentation rate and density was 0.68 $\text{g cm}^{-2}\text{a}^{-1}$. According to the average TP concentration in sediment, the average accumulation rate of the TP (PAR) was estimated to be 5.4 $\mu\text{mol cm}^{-2}\text{a}^{-1}$.

To assess the fraction of buried P in the lagoon, the P burial efficiency (PBE) was calculated using the following formula (Monbet et al. 2007a; Hou et al. 2009):

$$\% \text{ P Burial efficiency (PBE)} = 100 \times \frac{\text{PAR}}{\text{PAR} + \text{Fe}_{\text{active}} \times \frac{\text{MAR}}{R_{\text{Fe-P}} \times 55.8}} \quad (1)$$

where $\text{Fe}_{\text{active}}$ (ppm), the concentration of Fe oxyhydroxides extracted in sequential extraction which was estimated from the difference in Fe concentration determined by X-Ray before and after sequential extraction, is on average 10470 $\mu\text{g g}^{-1}$ and $R_{\text{Fe-P}}$, the molar ratio of Fe to ($P_{\text{reac}} + P_{\text{redu}}$) in the

first layer sediment, is 108. Based on the analytical data for $\text{Fe}_{\text{active}}$, $(\text{P}_{\text{reac}} + \text{P}_{\text{redu}})$ and TP in this study, the value of PBE was calculated to be 82% in the Lake Illawarra. The high value of PBE can be attributed to the high sediment accumulation rate and the high value of $R_{\text{Fe-P}}$. Although it has been shown that most of the P_{reac} fraction appears to be only temporarily sequestered at the high sediment accumulation rate (Monbet et al. 2007b) and the possibility cannot be ruled out that a fraction of P_{reac} might be released to water column if the sediment accumulation rate was less, or the reduction intensity was enhanced (Bhadha et al. 2010), there is actually only a limited possibility of the P_{reac} fraction in Lake Illawarra being released to the water column. The Langmuir model is often used to fit the P sorption data (Bhadha et al. 2010; Lillebø et al. 2012). Only when the amount of P sorbed by $\text{Fe}_{\text{active}}$ is much smaller than the maximum sorption capacity, can the Langmuir model be approximately simplified to a linear model. Therefore, the high value of $R_{\text{Fe-P}}$ and significant positive correlation between $(\text{P}_{\text{reac}} + \text{P}_{\text{redu}})$ and $\text{Fe}_{\text{active}}$ (for core B: $r = 0.97$, $n=7$, $P < 0.0003$; for core C: $r = 0.7$, $n=7$, $P < 0.05$) indicate that $\text{Fe}_{\text{active}}$ was far from the maximum P sorption capacity and able to further sequester the released P in Lake Illawarra.

4. Conclusions

This study shows that P present in the Lake Illawarra sediments occurs, on average, as P_{resi} (5-44%), P_{reac} (17-40%), P_{auth} (14-28%), P_{org} (1-10%), P_{redu} (2-33%), P_{ex} (2-8%) and P_{det} (1-5%). About half of the TP, which mainly consists of P_{ex} , P_{reac} and P_{org} , is stored in the sediment in relatively labile fractions, which ultimately suggests some release into the water column. The Fe oxyhydroxides play a dominant role in the P cycle in the sediments of this lake. This is supported by significant positive correlation between P_{reac} and reactive Fe and a negative correlation between P_{auth} and Fe. The estimated P burial efficiency was relatively high, up to 82%, owing to the high sediment accumulation rate and the high value of $R_{\text{Fe-P}}$. The profiles of TP and P_{org} showed two peak values with depth, which correspond to large scale agricultural activities and urban development, respectively. The changes in P_{org} concentrations with depth are most likely indicative of the changed flux of organic matter that was buried in the sediment with P.

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