Phosphorus Cycling between Sediment and Overlying Water in Ben Chifely Reservoir, Australia under Simulated Core Incubation

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ABSTRACT

The flux of soluble reactive phosphorus (SRP) was estimated under simulated oxic, anoxic and aerated conditions in sediment cores collected from two sites in a meso-eutrophic reservoir that differ in depth and limnological characteristics. Hypolimnetic accumulation and the concentration of P in various sediment fractions were also studied to determine the factors and processes influencing SRP flux at the sediment-water interface. The average release of SRP under anoxic incubation varied between 16 - 70 µmol/m^2/day and 20 - 94 µmol/m^2/day in shallow and deep-water sites respectively. On the other hand, SRP was almost entirely lost to the sediment during simulated oxic or aerated experiments. Temperature influence on P release from the sediment was significant and the increment is considerable at water temperature above 20^{o}C. The reservoir sediment contained a large proportion of iron and aluminum bound P (Fe and Al-P). Fe and P ratio in the sediment exceeded 15 indicating high retention capacity of P by the sediment. Besides, the high amount of Fe and Al-P in the sediment reflects redox dependent P mobilization. Therefore, management needs targeting retention capacity of the sediment and alteration of anoxic condition in the hypolimnion during warmer months.

1. INTRODUCTION

The Ben Chifley Reservoir (149^{o}33' E, 33^{o}34' S) is located 20 km south east of Bathurst in New South Wales, Australia (Figure 1) and is the primary source of potable water for Bathurst, a provincial city located in the Central Tableland of NSW with a population of about 39,000 (BRC, 2017). It was established on the Campbells River, a tributary of the Macquarie River of the Murray-Darling Basin in southeast Australia. The reservoir has a surface area of 2.2 ha with a maximum capacity of 30,800 mL when at full capacity. Average daily water flow released into the downstream river is 4.5 mL/day which flows into the Macquarie River (BRC, 2017).

Eutrophication has become the main concern when the first outbreak of blue green algae (BGA) occurred in the reservoir during 1991, and since then BGA appearance has been noticed every year especially during summer months (December – January).

The upper catchment is dominated by pasture agriculture and receives different management practices to reduce external inputs of nutrients particularly phosphorus (P) due to its ultimate control on fueling nuisance algal blooms (Schindler et al., 2012; North et al., 2014; Tammeorg et al., 2017). Artificial aerator is currently in operation at the deep water close to the dam wall and operates in day time during warmer months to destabilize the anoxia or hypoxia (Rahman et al., 2005). But the reoccurrence of BGA bloom in the reservoir suggests that the management practices in the upper catchment to reduce external loading of phosphorus may not be the only solution in restoring reservoir water quality if excessive internal loading exists (Finlay et al., 2013).

Soluble reactive phosphorus (SRP), released from the bottom sediments to the overlying water can influence phosphorus (P) concentration in the water column and eventually support BGA growth. Sediments are an important part of the lake ecosystem showing both source and sink of P (Wang et al., 2014). The source-sink properties of sediments are controlled by the adsorption-desorption mechanisms which are influenced by several factors such as temperature, pH, oxygen concentration at sediment-water interface, nutrient concentration in

overlying water, bacterial activity and bioturbation (Nyenje et al., 2010; McCulloch et al., 2013). Release and absorption of P between sediment and water column create a dynamic balance in water bodies (Wang and Liang, 2015). Thus analysis of fractional distribution of P is important to determine the prerequisites for its endogenous loading and can contribute valuable complementary information for predicting the role of sediment in lake water quality (Kangur et al., 2013).

In this paper we assess the limnological processes pertinent to the flux of P in bottom sediment of the Ben Chifley Reservoir. Special emphasis is placed on retention, hypolimnetic accumulation, speciation, and dynamics of P at the sediment-water interface (SWI).

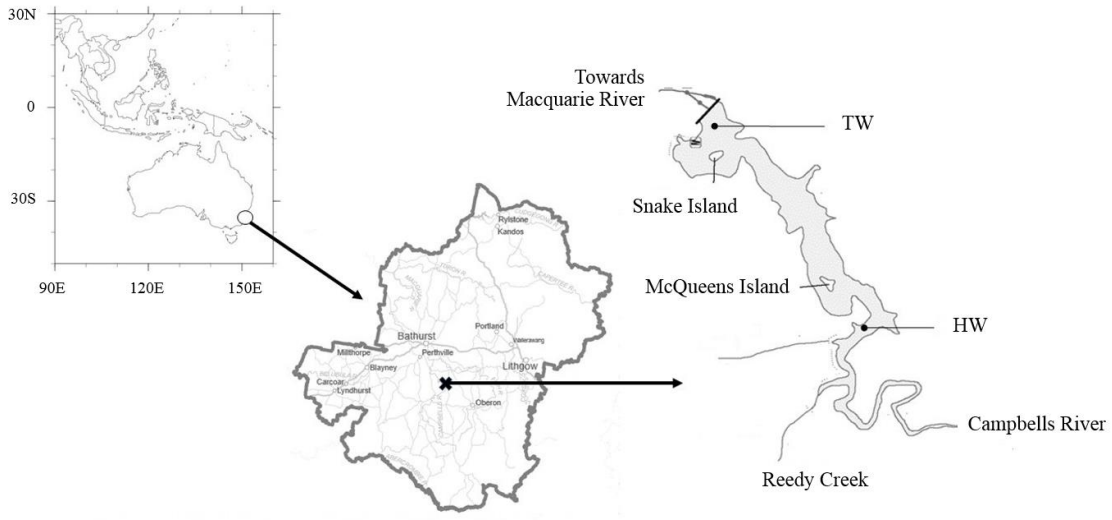


Figure 1. Location of Ben Chifley reservoir and two sampling sites, tail water (TW) and head water (HW).

2. METHODOLOGY

2.1 Sampling location

Two locations were selected for this study in head (HW) and tail water (TW) area of the reservoir (Figure 1). HW (Z_{max} = 6 m) is located at the reservoir inflow near the confluence of the Campbells River and Reedy Creek and the TW is located near the dam wall. TW is the deepest part (Z_{max} = 17 m) of the reservoir where the artificial aerator operates in day time during summer months. Triplicate sediment cores were taken from each site on two occasions during summer (December - February) and two occasions in autumn (March - May).

2.2 P fraction in sediment

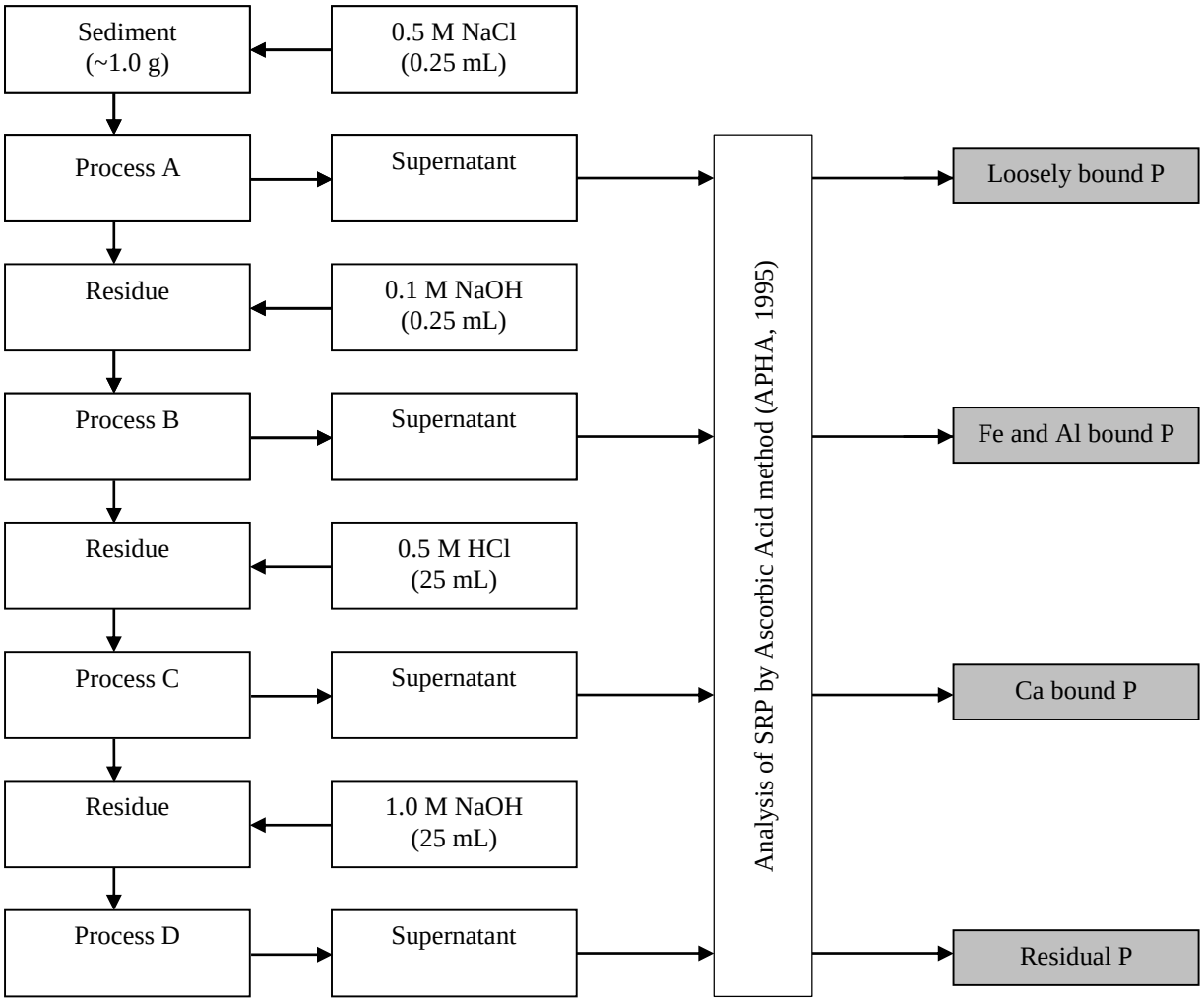
Triplicate cores were collected separately during the beginning of summer (December) from same sites for P-fraction analysis. Sediment cores were sliced at intervals of 1 cm (0 - 4 cm depth) and 2 cm (>4 cm depth) following Mudroch and Azcue (1995). A serial extraction procedure, adapted from Hieltzes and Lijklema (1980), was followed to extract different species of P from the bottom sediment (Figure 2).

2.3 Simulated core incubation experiment

2.3.1 Oxic environment

The sediment cores were set for a short period (4 h) of incubation under oxygenated and dark condition immediately after collection.

Water column in all of the sediment cores was flushed with the reservoir bottom water until the overlying water became clear to simulate the *in-situ* reservoir environment. Dissolved oxygen (DO) in the water column was measured by inserting HANNA (Italy) oxygen electrode at the beginning and end of incubation. Duplicate water samples were withdrawn from 4-5 cm above the SWI from each core for measuring initial and final SRP concentration.



Process A & C – 1.0 h incubation + Centrifugation for 20 min at 3600 rpm.
Process B – 18.0 h incubation + Centrifugation for 20 min at 3600 rpm.
Process D – 1.0 h incubation at 85°C + Centrifugation for 20 min at 3600 rpm.

Figure 2. Flow chart for the sequential extraction of phosphorus fraction in sediment.

2.3.2 Hypoxic or anoxic environment

Another set of triplicate cores collected from HW and TW were placed in a water bath and flushed with the bottom water at the University of Sydney Orange (USO) laboratory. Temperature in core water was maintained by aquarium thermostat at a level close to the bottom water temperature recorded during sampling. High purity N_2 gas was purged through the water column for creating anoxic/ hypoxic condition in the sediment core during 5-day experimental period. Aquarium thermometer was mounted on the wall of each core tube to monitor daily temperature of the water column. The temperature inside the cores was 20.5 ± 0.2°C during February experiment, 20.3 ± 0.4 in March experiment, 15.0 ± 0.5 in April experiment and 21.5 ± 0.2 in December experiment. The whole experimental unit was encased in black opaque polyethylene to minimize the effects of photo-synthesis. Duplicate water samples of 25 mL were withdrawn from each of the cores at 24 hours interval until the 5th day of incubation. The same volume of deionized water (purged with N_2 gas) was added after every time of sampling and the dilution factor due to the addition of deionized water was taken into account when water column SRP concentrations were measured.

2.3.3 Aerated environment

Triplicate sediment cores collected separately in December were incubated for 5 days under continuous aeration through a commercially available aquarium pump. Bubbling was done in such a way that the water column was well oxygenated without disturbing the surface sediments. The water column temperature throughout the experimental period was 20.5 ± 0.2°C which was very close to that of the reservoir bottom water (21.0 ± 0.2) recorded during the sampling day. Duplicate water samples (25 mL) were collected at 24 hours interval until 5th day of the experiment.

2.4 Chemical analysis

The water samples from each experiment were filtered through 0.45 µm filter and stored at 4°C until analysis. The concentration of SRP in water samples from each experiment was determined by flow injection analysis following the ascorbic acid reduction method (APHA, 1995). Total-Fe concentration in water samples from aerated incubation was analyzed by Perkin Elmer (USA) atomic absorption spectrometer.

2.5 Calculation of SRP flux

The SRP flux was calculated using the following equations (Lerat et al., 1990):

$$F = Q /(S \times T)$$

$$Q = E_1 + E_2 + ... + E_n$$

$$E_1 = E_{i+1} = (C_{i+1} - C_i) \times V_I$$

where, F= Flux (µmol/m^2/h), T = total incubation time (h), S = sediment surface area (m^2) and Q = total exchange during incubation period, E_{i+1} = exchange between T_i and T_{i+1}, V_i = water column volume (L), C_i = nutrient concentration at T_i (µmol/L) and C_{i+1} = nutrient concentration at T_{i+1} (µmol/L). According to this calculation, a negative flux is considered as uptake of SRP by the sediment whereas a positive value indicates release from the sediments.

3. RESULTS

3.1 Phosphorus fractions in sediment

The Fe and Al bound P and residual-P made up a large proportion of sediment P in both sites, accounting for 65-75% and 20-30% of the total P respectively. The loosely sorbed (adsorbed/bound) P was the smallest fraction forming less than 1% of the total P. Ca-bound P constitutes up to 3% of the total P in the reservoir sediments. Loosely sorbed P, Fe and Al-P and residual-P were significantly higher in the top few centimeters of the bottom sediments. The major two P species (i.e., Fe and Al-P and residual-P) in the sediment decreased with depth until 10 cm followed by a slight increase towards greater depth in both the sites (Figure 3). Declining in concentration of both common P species with sediment depth indicate the prominent activity of surficial sediments in recycling P. In contrast, the concentration of Ca-bound P was almost similar in both the sites (Figure 3).

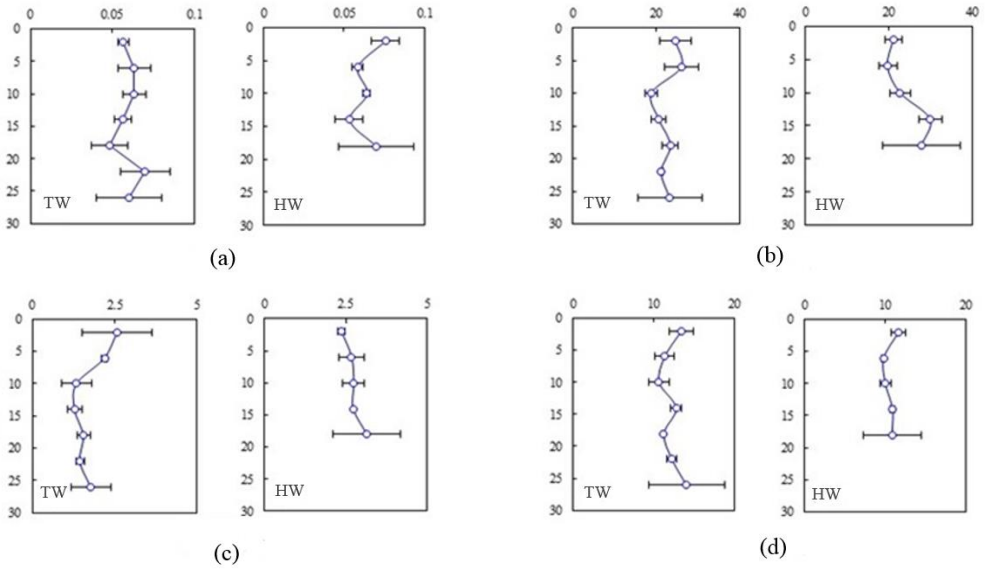


Figure 3. Depth distribution of P fraction (µg/g) in sediment cores collected from tail water (TW) and head water (HW). (a) Loosely bound P, (b) Fe and Al - bound P, (c) Ca - bound P and (d) residual P.

3.2 SRP flux from sediment core

3.2.1 Oxic environment

In net terms, the SRP was lost from the water column towards the sediment in oxic incubation. However, HW sediments acted as both sink and source of SRP under oxic environment regardless of the temperature or depth of the overlying water (Figure 4).

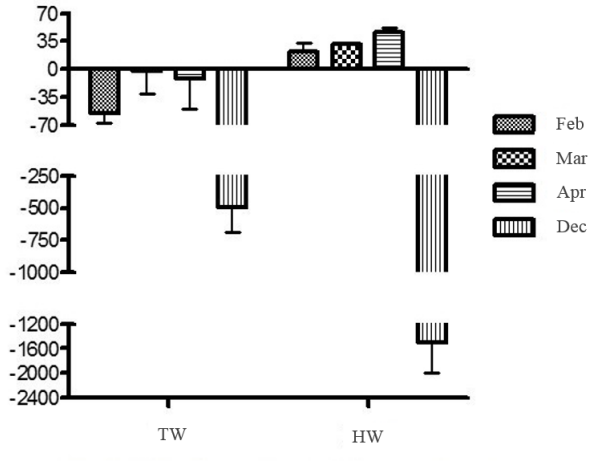


Figure 4. Flux of SRP (µmol/m^2/day) in sediment cores incubated under oxic environment.

The highest uptake of SRP was recorded in this shallower site from December experiment at the rate of 1,500 µmol/m^2/day. On the other hand, the February, March and April experiments at the HW site showed a relatively small SRP release from the sediments to the overlying water at the rate of 22 to 46 µmol/m^2/day. During these experimental periods, the TW site showed consistent trend of SRP flux from water to sediments with rates ranging from 3 µmol/m^2/day in March to 496 µmol/m^2/day in December (Figure 4).

3.2.2 Hypoxic/anoxic environment

With the establishment of hypoxic/anoxic conditions, the SRP was released from sediment to water column in all the cores. The two-way repeated measures ANOVA indicated that there was a significant effect of month (p = 0.032), which accounts for 40% (I^2 = 0.40) of the total variance (Table 1). SRP release rates in the sediment cores incubation conducted during summer (February and December) were slightly greater in TW site. The mean SRP release rate for the TW site during thermal stratification period was 61 µmol/m^2/day whereas; the HW site had a release rate of 54 µmol/m^2/day.

Table 1. ANOVA for SRP flux from the bottom sediments estimated from core incubation in different months.

Source of variation	SS	df	MS	F	P-value	F_{crit}	Eta square (I^2)*
Site	9.9E-05	1	9.9E-05	0.0883	0.7766	4.4940	-
Month	0.0134	3	0.0045	3.7679	0.0321	3.2389	0.40
Interaction	0.0009	3	0.0003	0.2488	0.8610	3.2389	-
Error	0.0190	16	0.0012	-	-	-	-

*$I^2 = SS_{month} / SS_{total}$

The maximum release was recorded in December in all the cores with the greatest release of 94 µmol/m^2/day observed in the TW site (Figure 5 (a)).

The incubation of the sediment cores conducted during autumn (March and April) showed a lower release of SRP varying between 16 to 47 µmol/ m^2/day. The release of SRP during December and February incubation experiment was significantly (α = 0.05, R^2 = 0.93) increased exponentially with core water temperature (Figure 5 (b)). Due to increased temperature, microbial activity in the sediment increases resulting in oxygen depletion and reduction of Fe^{3+} to Fe^{2+} with subsequent release of phosphorus bound to clay particles in the overlying water (Huang et al., 2011). The core water temperature during February, March and December incubation was between 20-21^{o}C whereas it was 15^{o}C in April incubation.

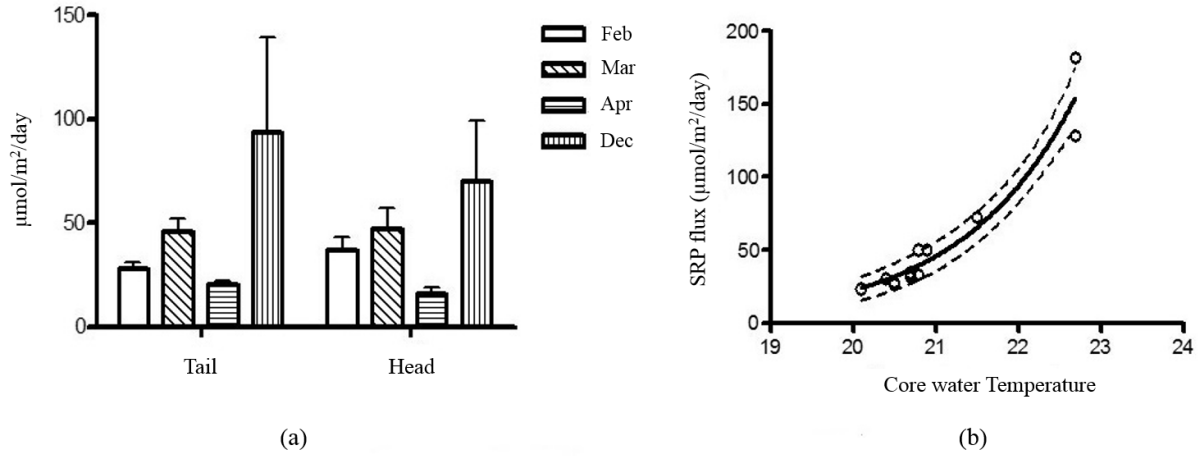


Figure 5. (a) Flux of SRP in sediment cores incubated under anoxic environment and (b) relationship between SRP flux and the temperature of overlying water in sediment core (dashed line represents 95% C.I).

3.2.3 Aerated environment

In aerated incubation, the cores were well oxygenated throughout the experimental period (120 h). The DO concentration at the end of incubation was between 5.7 mg/L to 7.6 mg/L in head water and 4.9 mg/L to 8.2 mg/L in tail water. Throughout the experiment the temperature inside the cores varied between 22.5ºC and 22.9ºC. The net SRP flux at both sites was from the overlying water to the sediment but the rate of uptake was higher in the HW site (173 µmol/m^2/day) than in the TW site (111 µmol/m^2/day). The maximum SRP uptake was recorded during the first 24 hours of incubation followed by slower uptake until 72 hours (Figure 6 (a)). Surprisingly, a release of SRP from the sediment to the overlying water, at the rate of 23 to 111 µmol/m^2/day was observed during the 96th hour measurement at both sites. The flux direction was then reversed back towards the sediments during the 120th hour measurement (Figure 6 (a)).

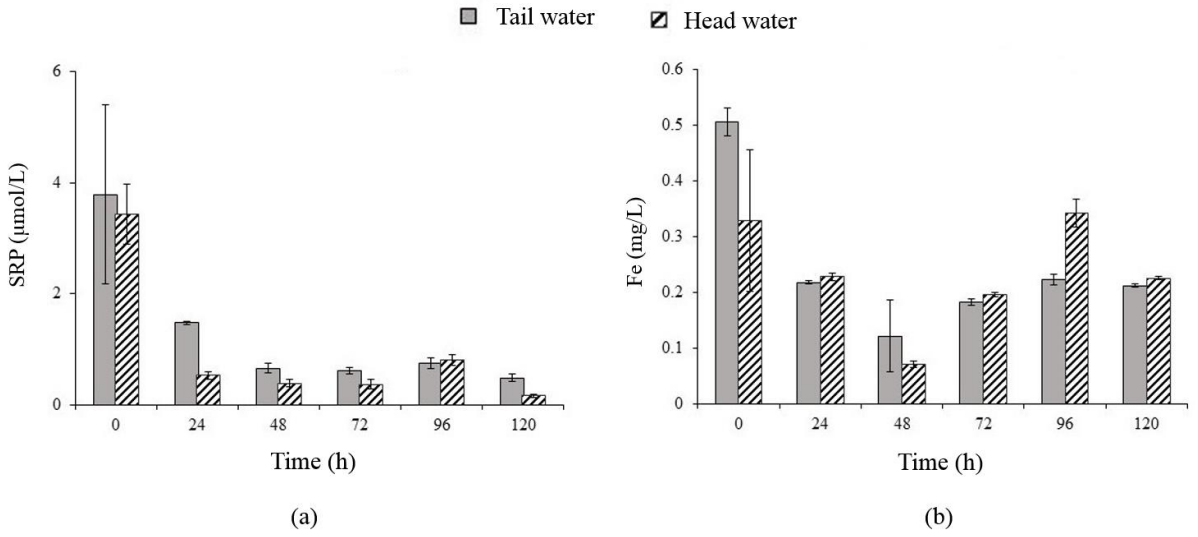


Figure 6. (a) Flux of SRP in sediment cores incubated under continuous aeration and (b) depletion of Fe from the overlying water in sediment cores.

This trend of SRP movement in dual direction across the sediment-water interface may have been influenced by the actual equilibrium conditions of available phosphorus between sediment and water (Niemisto et al., 2011). As a result of turbulent mixing and conversion of Fe^{2+} to Fe^{3+} due to oxygenation could be the cause of ultimate loss of reactive phosphorus from the water column (Khalil

and Riffat, 2013; McDaniel et al., 2009). The depletion of total soluble Fe from the water column was also observed in all the cores throughout the incubation period, which confirms the adsorption of phosphorus by iron (Figure 6 (b)).

4. DISCUSSION

Phosphorus fractions in the reservoir sediment were mainly dominated by Fe and Al bound P accounting for 65-75% of the total P. The high amount of Fe and Al-P along with the small proportion of loosely bound fraction of P reflects retention of inorganic P by Fe and Al and mobilization by the redox process (Kowalczewska-Madura et al., 2015). Experimental results from shallow lakes have shown that the retention capacity to be high as long as the Fe/P ratio (by weight) of the sediment exceeds 15 (Jensen et al., 1992). The average Fe/P ratio of the uppermost sediment layer (0-15 cm) in the Ben Chifley reservoir was twice as large as the above threshold value.

The average release of SRP from the sediments incubated under summer (February and December) anoxic conditions varied between 61 µmol/m^2/day and 54 µmol/m^2/day respectively. On the other hand SRP was almost entirely uptake by the sediment during all simulated oxic/aerated experiments. Exponential relationship between water temperature and SRP release from the incubation experiments during summer months suggested the temperature influence on P release in the Ben Chifley reservoir was significant. The increment is considerable at the core water temperature above 20^{o}C. The effect of temperature on P flux was highest in lakes with a large proportion of Fe-bound P where a decrease in thickness of the oxidized surface layer with increasing temperature was also noticeable (Jensen and Andersen, 1992). A statistically significant non-linear relationship was observed between Fe and Al-P content of the sediment and SRP flux in December experiment (Figure 7). SRP in the hypolimnion as a result of anoxic release is probably subject to chemical precipitation, biological uptake and re-deposition through particle sedimentation, and migration to the epilimnion through diffusion across the thermocline (Nowlin et al., 2005). However, it should be noted that the vertical diffusion of SRP from the hypolimnion to the epilimnion during summer months can be limited if strong thermal gradient was developed. Due to the absence of P input from the river-discharge during summer and autumn months, upward flux from the aerobic sediment surface could contribute a considerable proportion to the epilimnetic SRP concentration.

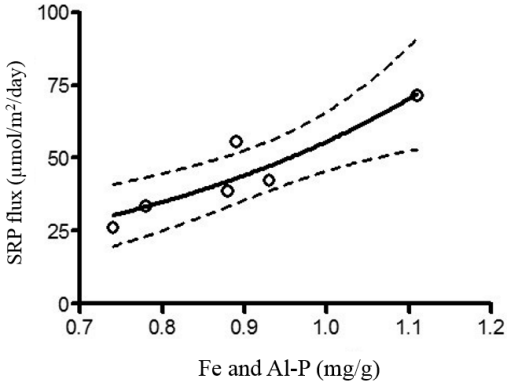


Figure 7. Correlation between SRP flux and the concentration of Fe and Al-P in the sediment core incubated under aerated environment (dashed line represents 95% C.I).

Though the overall SRP flux was mostly negative (downward) under oxic incubation, positive (upward) flux from the head water site (shallow depth) was recorded in February, March and April experiments. SRP release in an oxic environment could be due to higher pH values (>8.0) commonly observed in the overlying water of the reservoir in study. High pH in the overlying water triggers phosphate release by OH^- ion exchange with PO_4^{3-} on the surface of metal oxides-hydroxides (James et al., 1995; Niemesto et al., 2011). However, Fe(II) containing particles from the subsurface sediment layer can be re-oxidised to Fe(III) when there is a reduced redox condition and enhance P sorption potential (Lukawska-Matuszewska et al., 2013).

This pattern of SRP movement across the sediment-water interface reflects the dual role of sediments, i.e., uptake and regeneration of phosphorus. This dynamic also suggests that the littoral sediments can play an important role as a contributor to P budget in the reservoir.

When the bottom sediments are in contact with oxygenated water, re-oxidation of Fe^{2+} and re-adsorption of phosphate by ferric oxy-hydroxide can occur with net loss of bioavailable P from the water column to the sediments. Wind-induced mixing may significantly affect the P flux by increasing the contact between sediment and water and re-

suspending particulate P before being buried (Shinohara and Isobe, 2010; Wu and Hua, 2014) depending on the actual equilibrium conditions between sediment and overlying water (Hansen et al., 1997).

5. CONCLUSIONS

The sediments of Ben Chifley reservoir act as source and sink of phosphorus in different extent depending on the physico-chemical characteristics of the hypolimnion. The release of phosphorus from the bottom sediment is at most when anoxia develops in sediment water interface. The reservoir develops both thermal and oxygen stratification coupled with extremely low river-inflow during summer (Rahman et al., 2005) which triggers endogenous release of bioavailable phosphorus. Phosphorus fraction in the sediment is dominated by Fe and Al bound P and the release of this species of phosphorus mainly dependent on oxygen status in SWI, redox potential and temperature in overlying water. The average Fe/P ratio (by weight) of the uppermost sediment layer (0-15 cm) in the reservoir exceeds 15 (Rahman and Bakri, 2010) which suggests higher retention capacity of P (Jensen et al., 1992). Considering the release mechanism of phosphorus from the bottom sediment and the dominance of iron bound phosphorus fractions, the control measures could be focused on diminishing anoxia/hypoxia in the hypolimnion or demobilization of Fe and Al bound phosphorus.

Although hypolimnetic aeration through a mechanical device to diminish anoxia during summer months is in practice in the deepest part of the reservoir, but its effectiveness needs to be further investigated along with diurnal monitoring of temperature and oxygen profile. The chemical method aiming to influence the redox-dependent P fixation is another option which can be achieved by increasing the sorption capacity of the lake/sediment (Kowalczewska et al., 2015). Application of alum, Phoslock™, modified zeolite or more rarely, calcite, to increase the sorption capacity has been practiced in shallow lakes (Kleeberg et al., 2013; Zamparas and Zacharias, 2014). Removal of nutrient rich sediment by dredging could be another option which has been practiced in several countries (Sondergaard et al., 2003) depending on the economic feasibility. The effectiveness of those in-lake restoration measurements need to be studied by conducting experiments either in-situ or in the laboratory before being recommended the most suitable inactivation agent. But it is also to be noted that, the success and sustainability of in-lake restoration practices depends on the reduction of external phosphorus loading although it is time consuming and the success depends on various bio-physical and socio-economic factors in the catchment (Bakri et al., 1999).

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